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Guidance for the Collection and Use of Ambient Hydrocarbon Species Data in Development of Ozone Control Strategies

SRI International
Menlo Park, CA

Prepared for

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This document provides a standard set of procedures that can be routinely and reliably depended upon to obtain NMHC species composition of the ambient air. The document discusses the needs that exist for the quantification of ambient HC species, especially as they relate to air quality management applications. Procedures for site selection, sample collection and storage, calibrations and analysis, and quality assurance and control are described. State-of-the-art HC species analysis techniques are unable to identify 10 to 35 percent of the ambient NMHC burden. Recommendations are made to fill gaps in our current knowledge.

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GUIDANCE FOR THE COLLECTION AND USE OF AMBIENT HYDROCARBON SPECIES DATA IN DEVELOPMENT OF OZONE CONTROL STRATEGIES

Final Report

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Contract 68-02-2548

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Prepared for

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ABSTRACT

This document provides a set of standard procedures that can be routinely and reliably depended upon to obtain nonmethane hydrocarbons (NMHC) species composition of the ambient air. The document discusses the needs that exist for the quantification of ambient hydrocarbon (HC) species especially as they relate to air quality management applications. Procedures for site selection, sample collection and storage, calibrations and analysis and quality assurance and control are described. State of the art HC species analysis techniques are unable to identify 10 to 35 percent of the ambient NMHC burden. Recommendations are made to fill gaps in our current knowledge.

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EXECUTIVE SUMMARY

A measure of ambient hydrocarbon (HC)* composition is an essential input to air quality models used to determine HC reductions required to achieve the federal ozone (O_3) standard. To date, no standardized procedures for HC measurements in ambient air exist. The major purpose of this document is to describe and recommend a set of standardized procedures that can be routinely depended upon to provide reliable HC species data for air quality management. The detailed methods presented here, provide the best and simplest means for measuring ambient concentrations of total nonmethane hydrocarbons (NMHC),* structurally similar HC groups (e.g., alkanes, alkenes, aromatics), and individual HC species. It is not implied, however, that other methods are necessarily unreliable. This document also addresses the needs of air quality models, possible characterization of HC composition from limited species measurements (based on analysis of existing data), quality control procedures, and knowledge gaps.

Air quality models were examined to demonstrate that detailed HC species measurements provide a good means to satisfy some of the models' needs as well as other air pollution requirements. Continuous NMHC instruments that have been used in the past and satisfy the needs of the simplest models (such as EKMA) are considered unreliable at NMHC levels of less than about 1 ppm C. A great deal of ambient NMHC data in typical urban/suburban locations lies below 1 ppm C. The entire range of ambient NMHC concentrations (typically 0.1 to 3 ppm C) can be accurately measured only by HC species analysis. HC species data are also highly desirable because they allow HC reactivity comparisons, act as indicators of sources, and permit the determination of exposure to certain toxic chemicals (such as benzene). However, species measurements cannot be made continuously and require specialized instrumentation and personnel. For special modeling applications, especially in regions where ambient NMHC concentrations are above 1 ppm C, continuous instrumentation can be highly beneficial.

Figure 1 summarizes the sequence of events that occur during the conduct of HC species analysis. The overall task of HC species analysis can be broadly divided into the following categories:

- Site selection
- Sample collection and storage
- Instrumentation and analysis
- Quality control and assurance.

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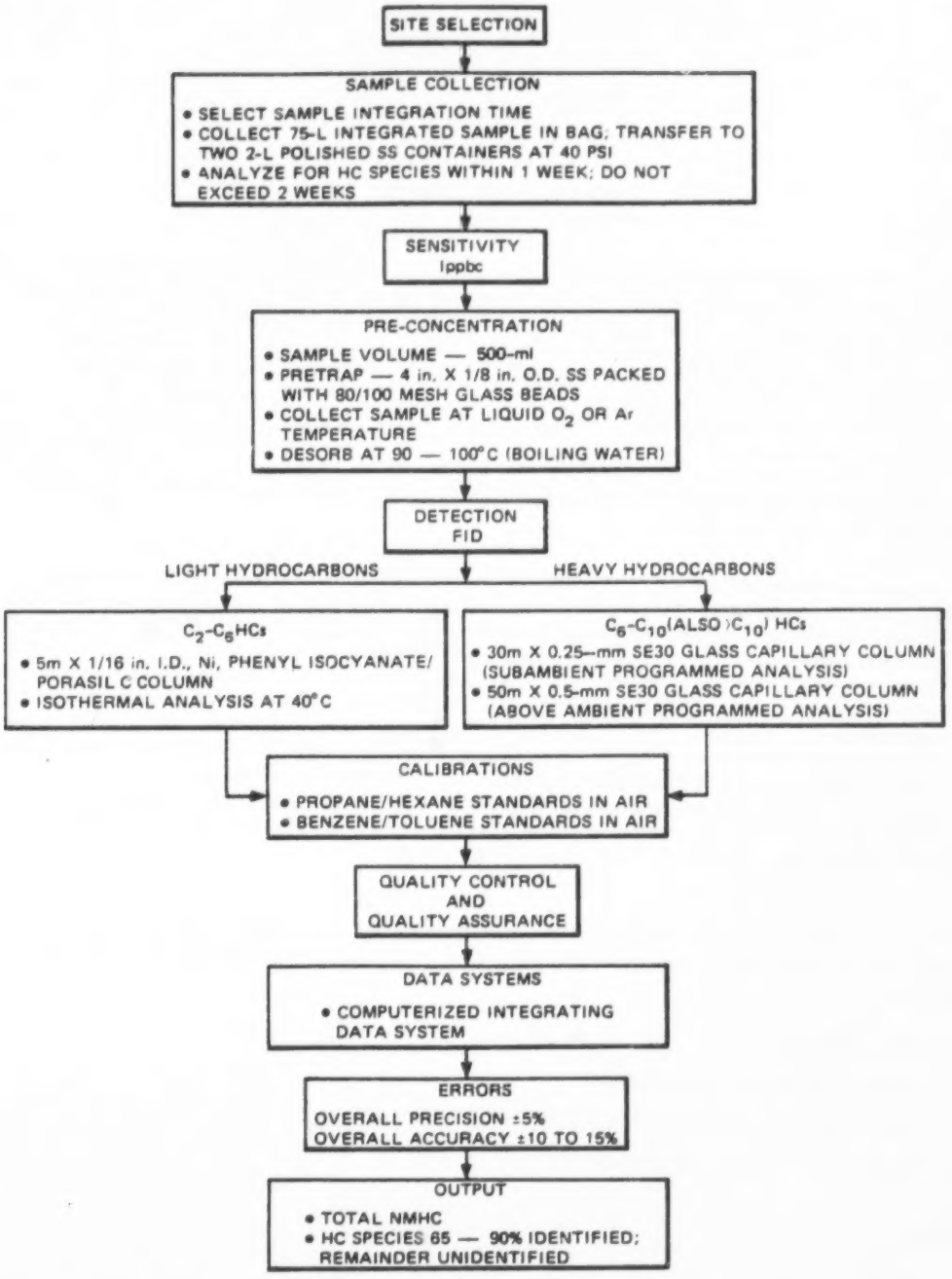
*The terms HC and NMHC can be used interchangeably with VOC (Volatile Organic Compounds) and NMOC (Nonmethane Organic Compounds), respectively, for the purposes of this document.


SITE SELECTION
SAMPLE COLLECTION
• SELECT SAMPLE INTEGRATION TIME
• COLLECT 75-L INTEGRATED SAMPLE IN BAG; TRANSFER TO TWO 2-L POLISHED SS CONTAINERS AT 40 PSI
• ANALYZE FOR HC SPECIES WITHIN 1 WEEK; DO NOT EXCEED 2 WEEKS
SENSITIVITY
1ppbc
PRE-CONCENTRATION
• SAMPLE VOLUME — 500-ml
• PRETRAP — 4 in. X 1/8 in. O.D. SS PACKED WITH 80/100 MESH GLASS BEADS
• COLLECT SAMPLE AT LIQUID O_2 OR Ar TEMPERATURE
• DESORB AT 90 — 100°C (BOILING WATER)
DETECTION
FID
LIGHT HYDROCARBONS
HEAVY HYDROCARBONS
C_2-C_6HCs
• 5m X 1/16 in. I.D., Ni, PHENYL ISOCYANATE/ PORASIL C COLUMN
• ISOTHERMAL ANALYSIS AT 40°C
C_6-C_{10}(ALSO >C_{10}) HCs
• 30m X 0.25-mm SE30 GLASS CAPILLARY COLUMN (SUBAMBIENT PROGRAMMED ANALYSIS)
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CALIBRATIONS
• PROPANE/HEXANE STANDARDS IN AIR
• BENZENE/TOLUENE STANDARDS IN AIR
QUALITY CONTROL AND QUALITY ASSURANCE
DATA SYSTEMS
• COMPUTERIZED INTEGRATING DATA SYSTEM
ERRORS
OVERALL PRECISION ±5%
OVERALL ACCURACY ±10 TO 15%
OUTPUT
• TOTAL NMHC
• HC SPECIES 65 — 90% IDENTIFIED; REMAINDER UNIDENTIFIED

Figure 1. Sequence of events for the collection and analysis of ambient HC species data.

Briefly, a site should be located away from areas having large source gradients and should be representative of as large an area as possible. Areas with strong source gradients would normally require a more intensive sampling network. The geographical representativeness of a site must be estimated. In general, open urban areas away from large and even small sources of HCs (e.g., refineries, gas stations, roadways, O_3 instrumentation) are preferred. The sampling air inlet sould be 3 to 15 m above ground level and at least 1 m above a support surface. Analysis of available information (e.g., maps and aerial pictures, population densities, land use, meteorological and climatological data, emissions inventories, existing monitors) and consultations with those responsible for selecting existing NMHC monitoring sites are a good practical approach to site selection.

Once the site has been selected, other details such as power availability and shelter should be established. A sample integration time (e.g., a 3-h, 1-h, or instantaneous sample) should be fixed before collecting the air sample. Stainless steel metal bellows pumps (MB-158, MB-151, MB-41, MB-21) are recommended for sampling. After considering several sampling methods a combination bag/metal container approach is recommended. A 75 to 100 liter, 2 mil Tedlar bag (or a 5 mil Teflon bag) provides an easy means to collect an intergrated (say, 3-h) sample. Such bags should be cleaned thoroughly before testing and kept in a cool (<70°F) and dark place before and during sampling. Once the Tedlar bags are filled, the air should immediately be transferred to two evacuated, 2-liter electropolished stainless steel canisters at 35 to 40 psi pressure (both canisters should be analyzed for detailed HC species). Prior to sample pressurization, these evacuated canisters (previously cleaned) should be flushed with the bag air (5 to 10 liters per canister should be sufficient) and reevacuated to ensure that any residual air is the same as that in the bag. All O_3 is essentially destroyed during these transfers and no nitric oxide spiking is considered necessary. For collecting instantaneous samples, the bag step (necessary for time integration) should be eliminated and stainless steel vessels pressurized directly.

Once collected, air samples should be analyzed as quickly as possible, but a 1 week delay may be tolerated. A delay of 2 weeks is unacceptable. C_2 to C_{10}HCs constitute the major identified fraction of ambient NMHCs. Typically, 10 to 35 percent of the NMHCs are unidentified in ambient HC species analysis. Because of the established flame ionization detector (FID) response to carbon, the concentration of unknown NMHCs can be quantified reliably, although this is not possible for oxygenated species, such as aldehydes, ketones, and acids.

For ease of analysis, it is desirable to divide HC species into two major categories, namely, light hydrocarbons (C_2-C_6) and heavy hydrocarbons (C_6-C_{12}). The entire NMHC species analysis can be performed on two gas chromatograph (GC) columns. For modeling purposes, a measurement sensitivity of 1 ppb C for individual HC species is considered acceptable.

The C_2-C_6 HCs are easily measured on a packed GC column (see Figure 1) operated under isothermal conditions. A sample size of 500 ml is more than adequate. Even under very humid conditions, water does not pose a problem with this sample size. A glass bead preconcentration trap held at liquid oxygen or liquid argon temperature is used to trap all HC species (except methane). Sample volume is measured by accurately monitoring the pressure of a stainless steel vessel connected to the freezeout trap exit. Desorption is accomplished by rapidly heating the preconcentration trap electrically or with boiling hot water (90-100°C). C_2-C_6 analysis under the recommended procedures should not be carried beyond n-hexane. Species such a 2-methylpentane and n-hexane are also resolved during the heavy HC ($> C_6$) analysis. This redundancy is desirable and provides a good internal check.

The complexity of the heavy HC mix requires the use of glass capillary columns for the desired resolution. A computerized data system is mandatory when capillary columns are used. An SE-30 glass capillary column is recommended for the analysis of heavy HCs. A sample size of 300-500 ml is adequate and no water or CO_2 interferences are observed. Only HCs in the C_6 to C_{10} region (including the natural terpenoid species) are identified. However, the recommended column would also measure HCs higher than C_{10}. For the present, these would be a part of the unknown HC fraction. Unidentified C_{11} and higher HC species typically constitute an extremely small fraction of the total unidentified HC burdens.

No methods currently exist for the reliable measurements of oxygenated species. Aldehydes have the potential to play a significant role in photochemical smog formation, even at very low concentrations, but they do not constitute a large fraction of the ambient HC mix (<5 percent). Interim procedures for the measurement of aldehydes are suggested.

Calibrations and quality assurance procedures are devised to ensure a precision of ±5 percent for individual species. Samples are collected in two canisters and analyzed in duplicate. Overall accuracies are limited by the use of average carbon response for calibrations because these can introduce an error of 5 to 8 percent. In addition, errors on the order of 5 percent in the preparation of primary standards are to be expected. This would result in an estimated overall accuracy of about 10 percent $[(8^2+5^2)^{1/2}]$.

It is strongly recommended that all calibration standards be referenced to the National Bureau of Standards (NBS) propane (in air) standard, which has an estimated accuracy of ±2 percent. For the C_2 - C_6 column, propane is the best standard. Hexane can be measured on both the light HC and the heavy HC columns and is a good crossover standard. Because ppm levels (e.g., 5 ppm in air) of benzene and toluene can now be stored in high-pressure aluminum cylinders for more than a year, these can conveniently be used as standards for the analysis of heavy HCs. An FID carbon response is an acceptable procedure for the quantification of the concentration of unidentified HCs within an error of 5 to 8 percent.* Calibration frequencies (twice a day, single point check; once a week, multipoint check) are recommended recognizing that FIDs are extremely stable and calibrations in some cases have remained unchanged over a period of several months. It is recommended that at least 5 percent and preferably 10 percent of the samples be sent for referee analysis.

Practical means to collect HC species data are suggested. A number of shortcomings in the ability to characterize the ambient HC mix are apparent. Gaps in current knowledge are identified and recommendations made to fill these gaps. Analysis of samples by contractors is recommended.

*This is generally not true of HCs containing oxygen (oxygenated species) and chlorine atoms (fluorocarbons, etc.).

SECTION 1
INTRODUCTION

Ambient hydrocarbons (HCs)* and nitrogen oxides (NO_x) are the primary precursors of ozone (O_3), a key constituent of photochemical smog. Current strategies for controlling photochemical air pollution depend on HC abatement as the primary means of control. A measure of ambient HC species concentration is an essential input to determine the HC reductions required to achieve the federal O_3 standard.

Currently, several strategies that employ empirical-kinetic or photochemical diffusion models are available for purposes of air quality management. However, there are no standardized procedures for obtaining reliable ambient HC data. The quality of hitherto available data has been variable at best and even poor at times. Therefore, it is essential to document reliable procedures for the collection and analysis of HC data with built-in quality control, in an easily usable form. This document describes a set of procedures that will allow the collection of high quality ambient HC data at a level of detail that is commensurate with the needs and objectives of the specific application. It does not summarize methods used by various research laboratories, but rather describes a method which can be depended upon for routine acquisition of relible HC species data. Other methods not recommended here are not necessarily invalid. A standardized method is highly desirable, however, to assure intercomparability of samples collected by different control agencies in different geographical areas.

*The terms HC and NMHC can be used interchangeably with VOC (Volatile Organic Compounds) and NMOC (Non-methane Organic Compounds), respectively, for the purposes of this document.

SECTION 2
OBJECTIVES

The first and foremost objective is to prepare a guidance document for use by state and local air pollution agencies that describes and standardizes the procedures for the collection and analysis of ambient HC species data for the purposes of air quality management. Other important objectives of this study are to:

- Determine the extent and nature of HC composition data needed to satisfy existing photochemical air quality models.
- Recommend means for the practical acquisition of HC species data.
- Identify gaps in current knowledge, define uncertainties associated with the best available methods, and recommend needed future research.

In addition field data have been analyzed to study if a select group of easy-to-measure HCs can be used to represent the total burden and the composition of a complex ambient mixture of air (Appendix).

SECTION 3

GENERAL APPROACH

The contents of this document reflect the cumulative experience of staff members at seven U.S. laboratories.Detailed information was sought on methods of collecting and analyzing ambient air samples for hydrocarbon species. These laboratories were requested to provide information in as much detail as possible, but only on species for which they had direct experience and felt confident of the reliability of their data. The following organizations were queried:

- Battelle Columbus Laboratories
- California Air Resources Board (ARB)
- EPA-Environmental Sciences Research Laboratory
- General Motors Research Laboratories
- Research Triangle Institute
- SRI International
- Washington State University.

After each group responded to the queries, key investigators were contacted individually for further discussions. This information was complemented with a review of relevant published literature. Based on the collected data, a set of recommended procedures was compiled dealing with siting, sampling and storage, analysis, and quality control. The task of accurately measuring HC species depends critically on the satisfactory conduct of each one of these four steps.

In addition, detailed HC species data from a total of 12 sites in Houston and the South Coast air basin were analyzed. The purpose of this limited analysis of data was to explore whether a few select HCs, which are easy to measure, might be used to represent the total NMHC burden and/or the distribution of ambient air at a given site. The possibility of simplifying the otherwise rather complex process of obtaining NMHC data for those specific applications that allow greater flexibilty was investigated. The result of this analysis is presented in the Appendix.

SECTION 4

UTILITY OF HC SPECIES DATA

There is general agreement within the scientific community that detailed HC species data are very useful in designing and evaluating the progress of air pollution control strategies. When reliable data can be obtained, they have the advantage of meeting many research and air quality requirements because:

- Detailed HC species measurements have the potential to provide the most reliable measure of HCs in ambient air. All other methods currently known (e.g., continuous NMHC measurements) are less accurate.
- Detailed HC species data satisfy many of the needs of most air quality models whether these require as inputs NMHC, alkanes, alkenes, aromatics, aldehydes, C_2H_4, or a combination of these chemical groups.
- HC mixtures of widely varying reactivities can be identified and their oxidant forming potentials studied.
- Detailed HC species data help to characterize and locate sources in an area and can be used to estimate contributions from these sources.
- Specific HC species (such as benzene) are toxic and determination of exposure to these species is vital to developing strategies for the control of hazardous chemicals.

Although detailed HC species measurements are needed and desirable, a number of practical considerations have prevented the widespread application of these techniques, including the following problems:

- Techniques for measuring HC species require expensive instrumentation as well as experienced operators.
- These techniques are not standardized and have been used almost exclusively by research groups.
- Until recently, few people were aware that the continuous NMHC analyzers, which are relatively easy to operate, generate unreliable data, at least when NMHC levels are less than 1 ppm C. Unreliable data can be a serious handicap in devising and enforcing sound control strategies. Continuous NMHC analyzers do have utility under special conditions when the ambient air is highly contaminated. However, they cannot be relied upon to provide accurate data over a wide range of NMHC concentrations that are typically encountered in the ambient air (0.1 to 3 ppm C).
- Species measurement techniques are not continuous and can not satisfy the needs of models that require continuous HC data.

The HC input requirements of all available models are summarized in Table 1. The following HC categories meet the requirements of all air quality models in current use:

- Total NMHCs
- Alkanes
- Alkenes
- Aromatics
- Aldehydes (formaldehyde and higher aldehydes)
- Ethylene.

In addition, species such as acetylene (C_2H_2) and fluorocarbons are valuable indicators of sources and degree of contamination. Because no analytical method currently allows the separate measurement of individual groups of HCs, the only practical solution is the analysis of all predominant HC species.

TABLE 1. AIR QUALITY MODELS AND THEIR HYDROCARBON INPUT REQUIREMENTS

Model		HC Input Required	Remarks
Type	Name		
Empirical-Kinetic	EKMA (EPA)*	Total nonmethane hydrocarbon (NMHC)	Model uses "NMHC," which is assumed to be a mixture of surrogate C_3H_6 and n-C_4H_{10}. The model is validated against the Bureau of Mines Smog Chamber data. User must specify the surrogate C_3H_6/NMHC and n-C_4H_{10}/NMHC and aldehyde/NMHC ratios. Default values for these ratios are 0.25, 0.75, and 0.05, respectively. These ratios gave the best fit to the smog chamber data but are otherwise somewhat arbitrary. EKMA is not recommended for absolute results but provides a useful means for relative comparisons between emission reduction and oxidant scenarios.
Lagrangian photochemical air quality models	DIFKIN (ERT)†	NMHC	Input is the aggregated concentration of NMHC. One of the parameters in the chemical package is adjusted according to the initial NMHC/NO_x ratio. This is a multilayered model.
	REM (PES)‡	C_3H_6 and a generic HC that represents all other non-olefinic hydrocarbons	Model has same generation as DIFKIN. It assumes a well-mixed vertical column (single layer).
	ARTSIM (ERT)	Alkanes, alkenes, aromatics, formaldehyde, and higher aldehydes	CH_4 is excluded from alkanes. Model is multilayered.
	ELSTAR (ERT)†	Alkanes, alkenes, aromatics, and aldehydes	CH_4 is excluded from alkanes. Model is multilayered.
	SAI model (SAI)§	Alkanes, alkenes, aromatics, and aldehydes	Both CH_4 and C_2H_6 are excluded from the alkanes group. C_2H_4 is assigned to aromatics. Model is multilayered.
Eulerian Grid cell photochemical models	SAI model (SAI)§	Same as SAI Lagrangian	Eulerian models are highly complex, expensive to operate, and require detailed input data preparation for study of test cases.
	IMPACT (F and S)**		
	SULFA 3D (ERT)†	Same as ARTSIM	SAI model, IMPACT and SULFA 3D are multilayered models.
	LIRAQ-2 (LLL)††	Alkanes, alkenes, and aldehydes	CH_4 is excluded from the alkane group. Aromatic compounds are assigned to alkenes or alkanes depending on reactivity. LIRAQ-2 is a single layered model.
Box models	EPA	Similar to SAI model	Model is used for exploratory modeling studies.

*EPA – Environmental Protection Agency
†ERT – Environmental Research and Technology
‡PES – Pacific Environmental Services
§SAI – Systems Applications Inc.
**F and S – Forms and Substance Inc.
††LLL – Lawrence Livermore Laboratory

SECTION 5

SITE SELECTION, SAMPLE COLLECTION, STORAGE, AND INTEGRITY

Before an analysis is conducted, the task of collecting the air sample must be satisfactorily performed. This task is divided into the following four major parts:

- Site selection
- Presampling considerations
- Sample storage and integrity
- Recommended overall sampling procedures.

A. *Site Selection*

Siting is an important aspect of any HC measurement program especially in areas that contain a large number of sources. These sources can be located very close and yet be so small that they often go unnoticed. They may also be diffuse, low level area sources or large point sources. This report does not provide detailed criteria for site selection (see Ludwig and Shelar, 1978), but does briefly discuss those practical considerations that greatly facilitate the process of site selection.

HC species ambient measurements for the purposes of air quality applications are best utilized when the following two major considerations are met.

- The selected site should be well removed from nearby large HC point sources to ensure a degree of homogeneity.
- The chosen site should be representative of a well defined geographical area.

Any site selection process should be preceded by a knowledge of the following factors:

- Identification of the region of specific interest
- Purpose to be served by the measurements
- Desirable features of a potential site.

Once these decisions have been agreed to, a background information base should be assembled. This data base typically should contain the following information, relevant to the preselected region:

- Maps and pictures, including an aerial view
- Land use
- Emissions inventories
- Population densities
- Traffic distributions
- Climatological and meteorological data
- Existing monitoring data.

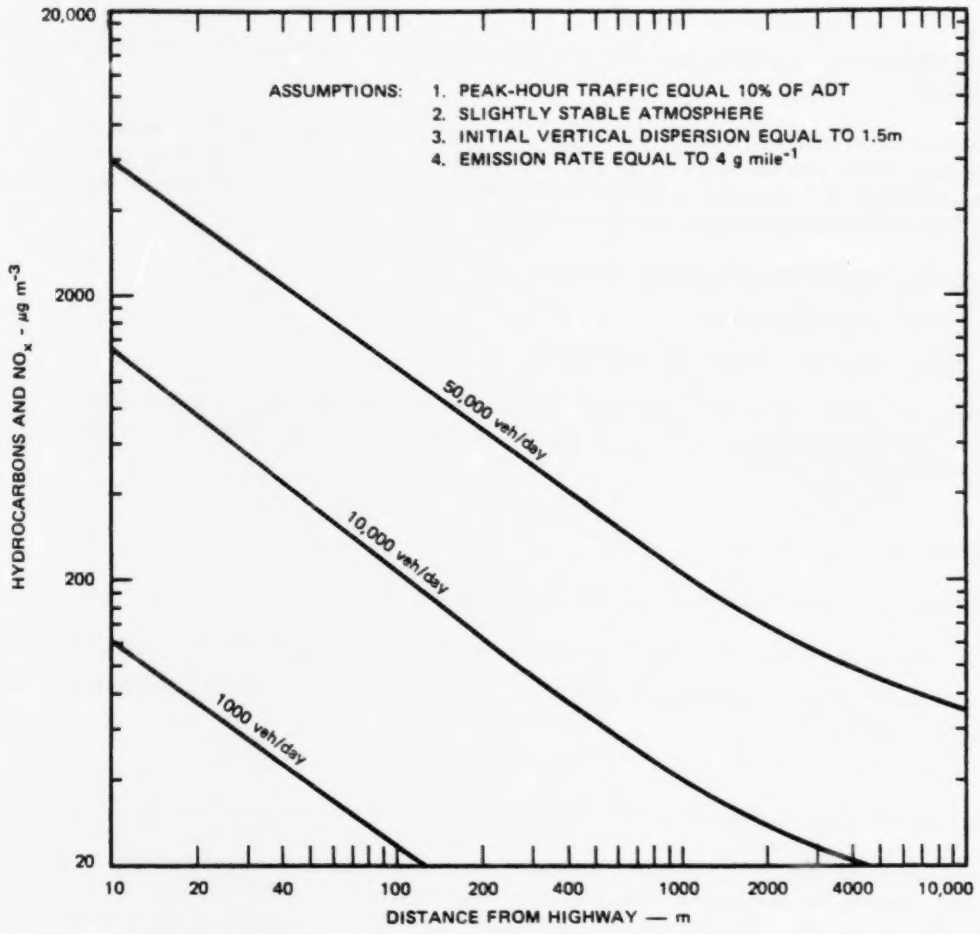
In practice, the task of selecting a desirable site is greatly facilitated by direct communication with those who were responsible for selecting existing HC monitoring sites. Often, available information from such sites is in itself a good indicator of the desirability of a given site. In general, the selection of a site should not be finalized until strong nearby sources are identified and their impact on the potential site assessed at least roughly. Regions of strong source gradients should either be avoided or enough sampling sites installed to characterize these gradients.

As a general rule, a site should be as well removed as possible from the impact of local sources. Five steps should be followed:

- Large point sources should be characterized and their impact on a potential site assessed using simple Gaussian models. It may be preferable to avoid sites that can be directly impacted by large point sources.
- A minimum separation from nearby roadways should be maintained. Figure 2 can be used to specify the separation (on a worst case basis) between monitoring sites and roadways with different levels of average daily traffic (ADT).
- A site should be as far removed as possible (at least several hundred meters) from such ground level sources as gasoline stations, drycleaners, surface coating operations, and refineries.
- The inlet of the sampling manifold should be 3 to 15 m above ground level (the higher the better) and at least 1 m above any support surface. In addition, it should be separated from surrounding obstacles by distances at least twice the height of the obstacle.
- An open urban location should be found. Street canyons should be avoided.

A problem sometimes encountered by researchers is contamination from other air quality instrumentation operating in the vicinity. For example, C_2H_4 from chemiluminescent O_3 analyzers has appeared in samples at concentrations of several hundred ppb's. Preferably, a sampling site should be well removed from and upwind of any air quality instrumentation. In addition, all ozone monitors should be fitted with C_2H_4 exhaust oxidizers.

In summary, selection of a proper site or sites should be made after a careful analysis of available information and consultation with those experienced in selecting monitoring sites. A



SOURCE: Ludwig and Shelar (1978)

Figure 2. Maximum roadway contribution to concentration at different distances.

knowledge of the performance of existing networks or air quality stations is a valuable guide in site selection. Guidelines such as those published by Ludwig and Shelar (1978) should be followed when specific applications are in mind.

B. *Presampling Considerations*

Once a site (or sites) has been selected, the task of sample collection begins. The operator must answer the following questions:

- What sample integration (averaging) times are required by the model?
- How much sample volume and how many samples are required?

- What kind of a sampling platform is to be utilized for ground level and/or airborne sampling?

Procedures recommended in this document for collecting air samples allow more than adequate sample volume for HC species analysis, are as applicable at ground level as aboard airborne platforms, and are easily adjusted to any sample averaging time. Integrated samples with the following averaging times are often needed:

- 3-hour integrated sample (e.g., 6 to 9 am)
- 1-hour integrated sample
- Instantaneous (or less than 10 min) sample.

Proper choice of a site when coupled with samples integrated over a long time period (e.g., 3 h) greatly increase the geographical representativeness of a sample. This is a desired goal in most air quality applications.

C. *Sample Storage and Integrity*

The most desirable features of a sampling vessel are:

- Its ability to contain an air sample without impairing its integrity for as long as possible.
- Its ability to allow collection of a desired volume of air sample with a preselected averaging time.
- Ease of handling and reliability of the vessel material.

The deterioration in integrity of an air sample because of interactions with the container walls frequently occurs during storage. In addition, the desorption of chemicals from walls of the container, permeation through walls (especially bags), as well as further reactions in the gas phase, need to be considered. The problem becomes especially difficult when a complex mixture is involved. Even though the total NMHC concentration is maintained, an internal chemical differentiation may occur. Additional steps are often necessary to minimize these problems. The two major sampling options available are:

- Collection of trace HCs on solid sorbent tubes
- Collection of whole air samples in bags and metal containers.

1. *Collection of Trace HCs on Solid Sorbent Tubes*

In principle, all trace constituents in the ambient air can be collected by passing air through a bed of a suitable solid sorbent maintained at a desired temperature. Typical sorbent materials used are charcoals, silica gel, alumina, and Tenax. The problems of collecting and retaining all components of a complex mixture of trace chemicals have not yet been resolved for any of these materials. Recently, Tenax (a polymeric material) has received the most attention because it can collect ambient species at room temperature. Low breakthrough volumes for water and CO_2 allow the preconcentration of HCs from extremely large volumes of air. However, many of the light HCs cannot be collected on Tenax. Overall, the advantages offered by solid sorbent traps do not outweigh their disadvantages. The advantages and disadvantages of cartridges in general and Tenax cartridges in particular are listed in Table 2.

TABLE 2. ADVANTAGES AND DISADVANTAGES OF SELECTED COLLECTION MEDIUMS FOR AMBIENT HC SPECIES ANALYSIS

Sampling Type	Advantages	Disadvantages
Solid sorbent tubes (Tenax)	• Adequate breakthrough volumes at ambient temperatures for some species • No significant retention of CO_2 and H_2O • Allows collection of very large sample volumes ($<10^4$ liters) for some species • Integrated samples over a period of minutes to days easily obtained • Thermal desorption of chemicals by heating at 400°C for several minutes easily accomplished • Sampling cartridges are light weight, low volume, rugged, and easily handled and transported	• Breakthrough volumes differ greatly and many species are only partially retained (see Table 3) • Serious artifact problems are encountered. Ozone and oxygen appear to oxidize Tenax, resulting in significant amounts of artifact contamination • In case of HC species analysis the major advantage of Tenax cartridges (collection of a very large volume) is not a necessary feature • Reduced precision due to less than quantitative collection and desorption of chemicals
Plastic bags [e.g., Mylar, FEP Teflon and Tedlar (PVC) films]	• Easy availability • Convenient for collecting integrated samples over any predefined time interval • Good stability of chemicals	• Poor handling properties, such as pinholes and cracks encountered during handling and transportation • Permeation of chemicals out of and into plastic film bags during storage • Self-contamination from compounds released due to outgassing from bag films
Passivated stainless steel canister	• Pressurization allows the collection of a desired volume of air ($\leq$ 20 liters) in a compact mode. • No chance of leakage or permeation of chemicals through metal walls. Sunlight is kept out. • Trace chemicals show excellent stability (see Table 4-6) • Easy to obtain, clean, transport, and handle	• Limited total volume can be collected ($\leq$20 liters STP) • Higher initial cost • Integrated samples not easily collected

Table 3 clearly shows that for many C_6-C_{10} HCs Tenax cartridges do not yield accurate quantification, which results in poor reliabilty. Results for C_2-C_5 HCs are even poorer. To date, the problem of artifacts remains poorly defined and highly unpredictable. Thus, cartridges filled wih solid sorbents (such as Tenax), at their present state of development, do not offer a desirable sampling means for the accurate quantification of hydrocabon species data.

TABLE 3. COMPARISON OF HC SPECIES ANALYSIS MEASURED DIRECTLY AND AFTER COLLECTION ON TENAX CARTRIDGES

Chemical Species	Tenax* ($\mu g/m^3$)	Direct ($\mu g/m^3$)	Ratio of Tenax/Direct
2-Methylpentane	12.8	23.7	.54
3-Methylpentane	8.4	16.5	.51
n-Hexane	11.7	20.4	.58
Methylcyclopentane	3.0	13.5	.59
2,4-Dimethylpentane	5.1	7.6	.67
Benzene	38.6	66.1	.58
Cyclohexane	5.2	6.2	.83
2-Methylhexane and 2,3-Dimethylpentane	13.2	24.5	.54
3-Methylhexane	6.4	12.6	.51
2,2,4-Trimethylpentane	7.7	13.5	.57
n-Heptane	7.7	13.6	.57
Methyl Cyclohexane	6.2	10.3	.60
Toluene	52.0	86.7	.60
2-Methylpentane	4.3	6.3	.68
3-ethylhexane	7.8	8.6	.91
n-Octane	6.5	6.6	.99
Ethylbenzene	13.7	13.5	1.01
m/p-Xylene	54.1	51.5	1.05
o-Xylene	20.9	19.3	1.08
n-Nonane	7.2	6.6	1.09
n-Propylbenzene	5.4	5.3	1.02
p-Ethyltoluene	21.1	19.5	1.08
m-Ethyltoluene	9.5	9.2	1.04
1,3,5-Trimethylbenzene	12.0	12.5	.96
o-Ethyltoluene	15.5	11.9	1.30
1,2,4-Trimethylbenzene	42.8	42.0	1.02
1,2,3-Trimethylbenzene	8.1	7.8	1.03
1,3-Diethylbenzene	9.8	9.2	1.06
1,4-Diethylbenzene	8.9	8.6	1.03
C-10 Substituted benzene	8.6	8.6	1.00

*500 ml sample air per gram of Tenax.

Source: Holdren et al. (1979)

2. *Collection of Whole Air Sampling in Bags and Metal Containers*

Collection of whole air samples is desirable when the volume requirements are less than 100 liters and preferably less than 25 liters. For the analysis of HC species, a 10-liter sample is considered to be more than adequate; thus, whole air sampling is an acceptable option. Two types of devices are commonly used for this purpose: plastic bags and metal containers.

For many years plastic bags have been used as storage and reaction containers for atmospheric photochemical studies. Although a wide variety of bag materials has been tried, the most common materials have been such commercial polymer films (2 to 5 mil) as Mylar, FEP Teflon, and Tedlar (polyvinyl fluoride material). The most desirable feature of the bags is their flexibility, which allows easy collection of an integrated sample. The major advantages and disadvantages of using these bags are summarized in Table 2.

The collective experience of all research groups supports the view that if the bags are handled carefully, they can provide a reliable means of collecting an air sample for HC species analysis. However, problems of outgassing and permeation into and out of the bags can create serious problems (see Seila et al., 1976). All the problems associated with bag sampling are greatly minimized by the following precautions:

- Checking to assure against a "bad batch" of bag material by flushing it with HC free air and analyzing the stored air.
- Thorough cleaning of bags.
- Storage of bags (before and after sampling) in dark areas and at relatively cool temperatures (<70°F).
- Sample storage times of less than one day.
- Careful and minimal handling of film bags.

Long-term storage in the bags or transport in bags of the sample from the field to central laboratories is at best an undesirable practice. Although some have claimed that bags yield reliable answers over a 2-week period, this delay is not recommended. Certainly, fluorocarbon tracers and several HCs are expected to permeate (both ways) through bag walls. For storage times of several hours, both outgassing and permeation problems are minimal. The flexibility with which bags can be easily used to collect whole air integrated samples is their major asset.

Because of the shortcomings of bags, solid wall containers have become increasingly popular in recent years. Glass, spectra-sealed aluminum, and stainless steel sampling canisters are available. Currently, the reliability of anodized aluminum cylinders for purposes of HC species sampling is uncertain and glass samplers can break. The most desirable sampling devices are passivated stainless steel canisters. Electropolished by the SUMMA process (patented), these lightweight containers can be safely pressurized to 50 psi. A 2-liter canister weighs less than 1.5 kg. Figure 3 shows a 1-liter passivated sampling canister. These are available in 0.5 to 6 liter sizes in cylindrical or spherical shapes. A 2-liter size is considered optimum for detailed HC species analysis.

The advantages and the disadvantages of these metal containers are listed in Table 2. The major disadvantage of these canisters is the inability to collect an integrated sample in a

Figure 3. Specially treated 1-liter stainless-steel sampling vessel for collecting grab samples

reproducible fashion. * For collecting instantaneous grab samples (i.e.,sampling time less than 10 minutes), the metal container can be directly pressurized. It is clear from Table 2 that the major disadvantage of metal containers—the inability to collect an integrated sample—is precisely the advantage that the bags offer.

Polished stainless steel containers (PSSC) have been extensively tested with satisfactory results by virtually all research groups. Tables 4 and 5 show the stability of C_2 to C_5 and C_5 to C_{10} HCs, respectively, in these sampling vessels for periods of 1 to 3 weeks. In addition, the stability of selected natural HCs in these canisters is evident from Table 5. Similar resuls in Tedlar bags have also been reported by Lonneman and Bufalini (1979). Table 6 further shows that oxygenated species are also stable in these canisters. Other tracers, such as fluorocarbons-12 and 11, have maintained their integrity in these canisters for several years (Singh et al., 1979).

D. *Recommended Overall Sampling Procedure*

Clearly, metal containers provide all the desirable features of a sampling vessel, except for the ability to directly and easily collect a linearly integrated sample of air. This, however, is the best feature of bags. Therefore, a combination bag/metal container approach for sample collection is recommended. This approach draws on the best features of both sampling options.

Any sampling procedure must be tested to ensure that no contamination of air occurs at any step. Bags and polished stainless steel containers must be specially and thoroughly cleaned before any sample collection begins. The PSSC are best cleaned by heating them at 100°C and purging them with cryogenically cleaned (at liquid O_2 temperature) ultrapure air at a flow rate of 0.5 liter per minute for a period of approximately 30 minutes. Purging with an inert gas such as helium or nitrogen is not quite as effective. The effectiveness of air is partly due to the oxidative properties of oxygen. In actual practice, two or three of these canisters can be connected in series to save time and gas. After this cleaning process, the PSSC should be stored under a positive pressure. Other cleaning processes, where heated canisters are filled with clean air and then evacuated, with the procedure repeated several times, are also acceptable. Depending upon the number of samplers, ten or more PSSC can be cleaned simultaneously.

In the sampling procedure very few bags are required; two or three bags per site are adequate. Whenever possible, 75 to 100 liter bags (2 mil Tedlar or 5 mil Teflon) should be used. These bags must be individually and thoroughly cleaned. The bags should be filled with ultraclean air and evacuated. This procedure should be repeated several times until the bags are clean.

In summary, the following overall steps in sampling are involved:

- Select a sample integration (averaging) period.
- Procure a 75 to 100 liter bag that has been previously cleaned and protect it from sunlight.

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*Attempts have been made to directly collect integrated samples in metal containers (Harden, 1979). An evacuated vessel is slowly filled by using a critical orifice that controls flow. This results in a non-linearly integrated sample since the flow rate varies as the backpressure increases. Therefore, this technique cannot be recommended for quantitative and accurate HC species analysis.

TABLE 4. STABILITY OF SELECTED LIGHT HCs (C_2-C_5) IN PASSIVATED STAINLESS STEEL CONTAINERS

Sample Number	A-84				A-176				A-190					
Date of Collection	7/6/78 (0730-0910 EST)				7/6/78									
Date of Analysis	7/7	7/7	7/18	7/25	7/6	7/7	7/18	7/25	7/6	7/6	7/18	7/25	Mean	Standard Deviation
Ethane	12.8	13.2	13.6	13.0	13.3	12.4	12.4	11.9	12.7	13.8	12.7	12.5	12.9	0.5 (≈4%)
Ethylene	104.8	103.5	98.2	100.5	102.5	99.0	94.6	97.9	108.9	106.6	100.4	103.1	101.7	4.0 (≈4%)
Propane	6.2	6.6	7.1	6.6	6.0	5.8	5.0	6.3	6.0	6.6	6.4	6.0	6.2	0.5 (≈8%)
Acetylene	138.1	136.9	126.6	119.4	149.0	130.2	124.5	120.3	149.5	142.2	131.2	127.8	133.0	10.2 (≈8%)
Isobutane	7.0	9.1	6.3	7.6	7.8	6.2	7.4	8.7	10.4	6.4	7.5	7.6	7.7	1.2 (≈15%)
n-Butane	38.6	38.8	34.6	37.2	38.7	35.8	35.1	36.0	40.4	38.0	38.8	36.9	37.4	1.8 (≈5%)
Propylene	34.3	31.3	28.6	28.6	32.3	29.5	27.0	27.7	35.8	34.1	31.3	31.2	31.0	2.8 (≈9%)
Isopentane	65.1	59.3	58.5	56.3	62.3	60.0	55.4	55.8	61.0	61.2	55.1	59.5	59.1	3.1 (≈5%)
Pentane	44.3	42.2	40.5	37.6	38.5	38.1	38.3	45.1	42.4	32.7	39.0	38.4	39.8	3.4 (≈8%)
Sum	451.2	440.9	414.1	406.8	450.5	417.0	399.7	409.7	467.1	441.6	422.4	423.0	428.7	21.0 (≈5%)
Mean	428.2				419.2				438.5				428.6	9.7 (≈2%)
Standard Deviation	21.2 (≈5%)				22.0 (≈5%)				21.0 (≈5%)					

Source: Harden (1979)

TABLE 5. STABILITY OF SELECTED HEAVY HYDROCARBONS (C_5-C_{10}) IN PASSIVATED STAINLESS STEEL CONTAINERS ($\mu g/m^3$)

Compound	Initial Concentration	Concentration After 1 Week	Percentage Change	Concentration After 2 Weeks	Percentage Change	Concentration After 3 Weeks	Percentage Change
2-Methylpentane	6.0	5.9	−2%	5.7	−5%	5.4	−10%
3-Methylpentane	3.7	3.8	+3	3.9	+5	3.6	−3
Hexane	5.6	5.2	−7	4.9	−13	4.7	−16
Methylcyclopentane	3.3	3.2	−3	3.1	−6	3.0	−9
2,4-Dimethylpentane	2.0	2.0	0	1.9	−5	1.8	−10
Benzene	6.7	6.2	−7	5.9	−12	5.4	−19
Cyclohexane	1.3	1.3	0	1.2	−8	1.1	−15
2-Methylhexane	7.5	7.0	−7	6.9	−8	6.4	−15
3-Methylhexane	3.0	2.8	−7	2.6	−13	2.5	−17
Dimethylcyclopentane	5.9	5.8	−2	5.6	−5	5.1	−14
2,2,4-Trimethylpentane	2.7	2.9	+7	2.5	−7	2.1	−22
Methylcyclohexane	2.0	1.8	−10	1.7	−15	1.7	−15
Toluene	14.8	14.3	−3	13.7	−7	11.9	−20
2-Methylheptane	1.9	1.8	−5	1.8	−5	1.6	−16
3-Methylheptane	1.3	1.3	0	1.3	0	1.2	−8
Octane	1.0	1.0	0	1.0	0	.9	−10
Ethylbenzene	2.5	2.5	0	2.4	−4	2.1	−16
m, p-Xylene	10.1	10.1	0	9.7	−4	8.4	−17
o-Xylene	3.4	3.3	−3	3.4	0	3.0	−12
4-Ethyltoluene	2.5	2.5	0	2.4	−4	2.6	+4
2-Ethyltoluene	2.2	2.0	−9	1.8	−18	1.6	−27
1,2,4-Trimethylbenzene	3.9	4.0	+3	3.9	0	2.9	−26
1,2,3-Trimethylbenzene	3.9	3.3	−15	2.8	−28	2.4	−38
Isoprene*	26.4	25.4	−4	23.9	−10	21.9	−17
α-Pinene*	13.1	11.9	−9	9.6	−27	5.3	−60
β-Pinene*	9.4	7.9	−16	5.6	−40	2.5	−73
Limonene*	8.4	6.1	−27	1.0	−88	<1.0	−100

Source: Holdren et al. (1979)

*Canister artificially spiked with these compounds.

TABLE 6. STABILITY OF SELECTED OXYGENATED SPECIES IN PASSIVATED STAINLESS STEEL CONTAINERS

Compound*	Percentage Change After 3 Weeks Storage		
	Can 1	Can 2	Can 3
Acetone	+10	+13	+12
Neohexane†	0	0	0
Butyraldehyde	- 7	-17	-27
2-Butanone	+ 9	-14	-19
Crotonaldehyde	+ 9	- 6	- 9
Valeraldehyde	- 2	-31	-35
2-Pentanone	+10	- 1	+ 2
Furfural	- 2	-22	-49
2-Heptanone	+15	-13	- 7
Heptaldehyde	+ 6	-50	-76
Benzaldehyde	+ 6	-14	-13
2-Octanone	+10	-46	+24

Source: Holdren et al. (1979).

*Individual concentrations varied between 20 and 40 $\mu g/m^3$.

†Internal standard.

- Fill this bag at a constant flow rate so that a 70-liter air volume is collected over the selected averaging period.
- Transfer this bag air sample into two previously evacuated 2-liter PSSC at atmospheric pressure and evacuate these PSSC. Repeat this procedure twice (to ensure that any remaining air in the container has the same composition as the bag air).
- Fill the two containers with bag air at 35 to 40 psi pressure.

For each integrated sample collected in a bag, two separate canisters should be pressurized. While one 2-liter canister at about 40 psi is adequate for complete HC species analysis, quality assurance is greatly facilitated by collecting two canisters. Sample containers prior to sampling should be maintained at a positive pressure. The evacuation should be performed at the field site.

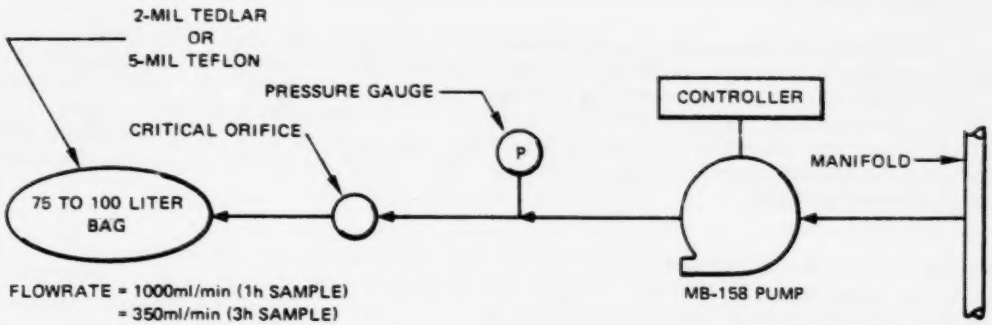
It is recommended that tubing employed during sampling should be precleaned stainless steel or Teflon. All fittings should be stainless steel, brass, or glass. Pumps for pressurizing and collection have been known to be key causes of contamination. Metal bellows (MB), Carbon Vane, and Komhyr "all Teflon" pumps are acceptable (Westberg, 1979). Metal bellows

pumps, in particular, the MB-158, a stainless steel pump that has all the features that a typical sampling program may require, is recommended. These metal bellow pumps can be used to pressurize sampling containers to 50 psi (typically 40-50 psi). Both battery operated and AC pumps are available. When an AC pump is being used, a long cord (200 m) must be carried for contingencies. The same pump (MB-158) can be used for evacuation of canisters. The canisters should be evacuated to as low a pressure as possible. Whenever a manifold is used for drawing inlet air, glass or stainless steel manifolds are desirable.

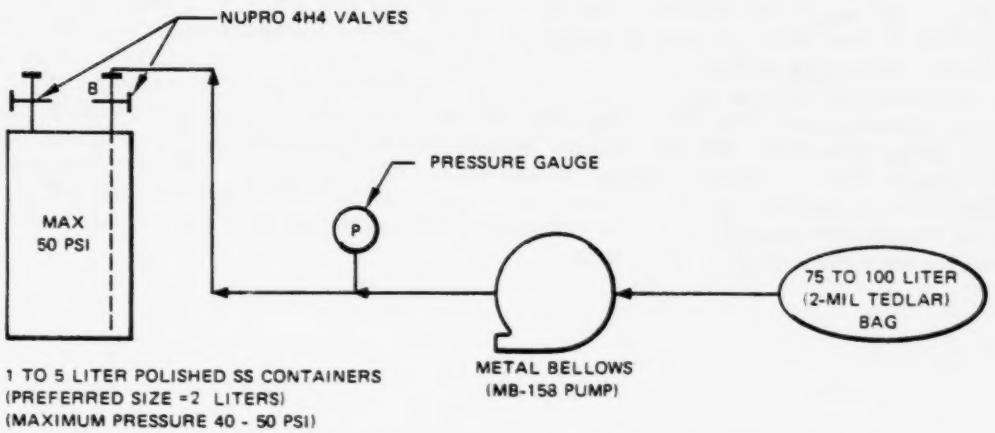
Self-contamination from pumps, tubing, valves, and containers is an important problem that can also vary widely depending upon the source as well as the batch of materials. No shortcut to a systematic evaluation of potential problem areas exists. It is recommended that ultrapure air be sampled through the entire sampling system and be analyzed before and after collection to ensure the cleanliness of the many parts that routinely constitute a sampling system. The same procedure should be used with a complex HC mixture (containing alkanes, alkenes, aromatics, etc.) to ensure that there are no surface removal problems.

Figure 4 provides a schematic diagram of an integrated bag sample collection and its transfer to the sampling container. A controller can be used to shut off the pump at the end of the selected sampling period. This could also be accomplished manually. Once the two samples have been collected, they should be completely labeled (sampler numbers, date, start time-end time, location, etc.) and stored for analysis.

It has been suggested often that sampling of alkenes, which are known to react with O_3, is best performed when the O_3 is quickly destroyed. Injection of NO has been used to effect this destruction. As long as the bag is kept in a dark place, O_3 generation from NO_2 photolysis (also generated from NO injection) can be eliminated. Practical experience indicates that this approach is unnecessary. For short integrating periods (<3 h), there is insufficient time for reaction during collection. Also, most pumps, including the one recommended here, destroy more than half of the O_3 during sampling; the bag surface destroys some more (Lonneman and Bufalini, 1979). A second transfer into a canister ensures almost complete destruction of O_3. Thus, for the sampling procedure recommended here, the injection of NO to destroy O_3 is considered unnecessary and could be omitted.



(a) INTEGRATED BAG SAMPLE



(b) INSTANTANEOUS TRANSFER FROM BAG TO CONTAINER

NOTE: All tubing should be stainless steel (SS) or Teflon; connectors and valves should be SS, brass, or glass.

Figure 4. Collection of integrated bag sample and transfer to metal container.

SECTION 6

ANALYSIS OF HC SPECIES

The analysis of HC species is often the most critical step, requiring sophisticated instrumentation and experienced personnel. A set of procedures that can be depended upon to provide detailed HC composition data for air quality management are described here. These procedures are kept as simple as possible while still reliably determining the composition of a highly complex mixture of ambient air. A detectability limit of 1 ppb C for individual species is assumed to be adequate.

A. *Mode of Operation*

As stated earlier, once samples have been collected, the delay between collection and analysis should be kept to an absolute minimum. This delay should be kept to an absolute minimum, not to exceed 1 week. Two modes of operation are generally feasible:

- An instrumented mobile laboratory is stationed in the vicinity of the sampling site.
- Samples are transported, sometimes over long distances, for analysis at central laboratories.

The first method is clearly the most desirable. Depending upon the number of samples, analysis time can be kept down to less than a day or two. Also, any problems or local features indicating hitherto unknown compounds are identified quickly and corrective action can be taken. The major disadvantage of stationing an instrumented field laboratory is usually the expense involved. However, this mode of operation should always be considered and used when feasible.

Because the practical needs of air quality monitoring far exceed the availability of instrumented mobile laboratories, the samples must often be analyzed at specialized laboratories. The major delay is usually transportation. However, through proper planning these delays can be minimized and kept to less than 1 week.

B. *Instrument Optimization, Sample Preconcentration and Injection*

While many sophisticated tools such as GC-MS have been used for the identification of ambient HCs during the developmental phases of measurement technology, the GC-FID techniques are considered satisfactory and the most practical means for HC species data collection. The flame ionization detector (FID) is a well-established and highly stable detector that possesses a remarkable linear dynamic range of 10^6. In addition, a unique advantage of the FID is its near linear response to the number of carbon atoms in organic compounds. Thus, calibrations do not have to be conducted for each and every species being

measured, and unknown peaks can be quantified. The GC-FID provides the best and most economical commercially available means for the analysis of HC species.

Instruction manuals for GC equipped with FID detectors usually describe the conditions for optimum analysis. These conditions, however, vary with the design of the FID. The operator is advised to consult the GC-FID manual for selection of optimum parameters. Table 7 shows optimum operating conditions (fairly typical of most FIDs) for the Hewlett-Packard Model 5711 A FID detector.

TABLE 7. OPTIMUM OPERATING CONDITIONS FOR MODEL 5711A (Hewlett-Packard) FID

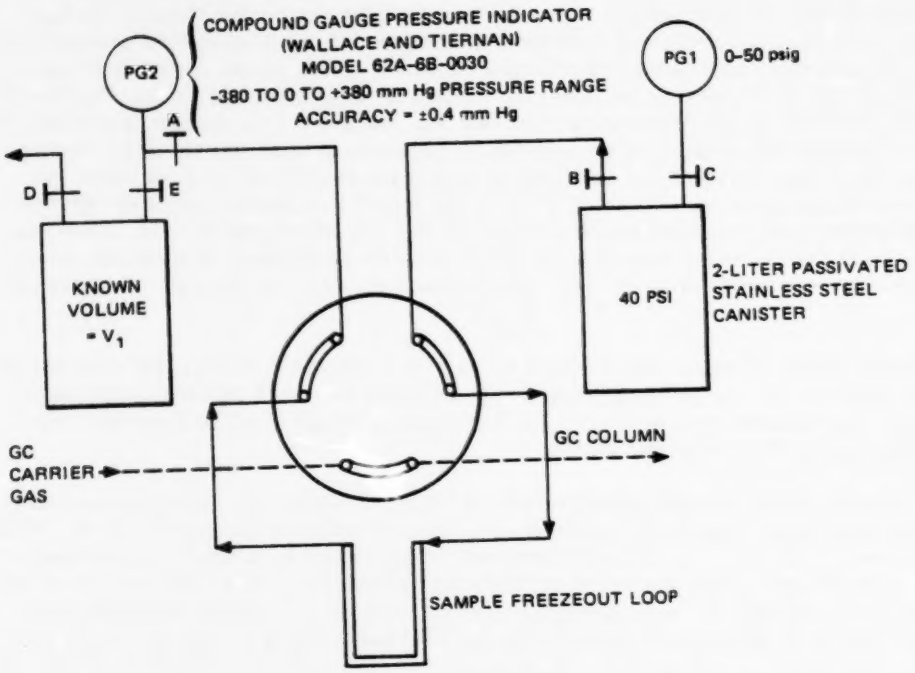
	Nitrogen Carrier	Helium Carrier
Total Carrier Flow*	51 ml/min	56 ml/min
Hydrogen Flow (20 psi)	39 ml/min	34 ml/min
Carrier/Hydrogen Ratio	1.31	1.62
Air Flow (20 psi)	240 ml/min	240 ml/min

*Auxiliary carrier gas must be added to the detector when the column flow is below this value.

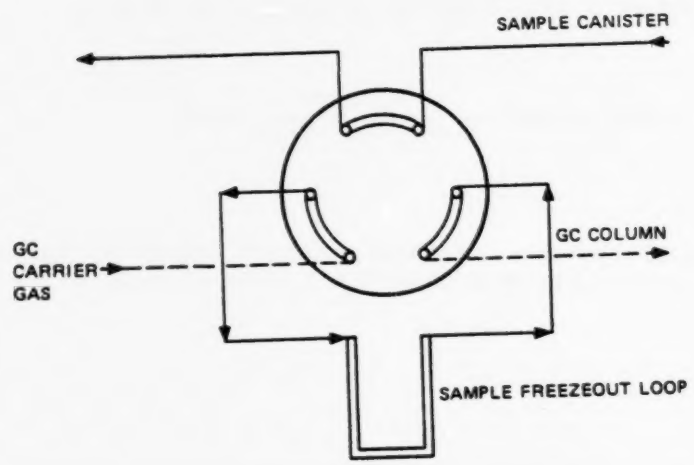
For a sensitivity approaching 1 ppb C, a 500-ml air sample is considered optimum. This will allow measurement of C_2-C_{12} HCs without causing problems due to clogging from water and CO_2. To inject a 500-ml sample of air, the HCs must be trapped on a sorbent material, which will allow the quantitative collection of all trace species without contamination and will desorb them quantitatively and easily. A 4-inch long bed of 80/100 mesh glass beads packed in an 1/8 in. o.d. stainless steel tubing serves as an excellent preconcentration trap for all HCs of interest. Although a 0.5-liter sample size is recommended, doubling this is not likely to create any problems. A 0.5-liter sample under extremely humid conditions (relative humidity > 90 percent) is easily retained on such a preconcentration trap.

Sample preconcentration is accomplished at liquid oxygen (B.P.-183°C) or liquid argon (B.P.-186°C) temperatures. Liquid argon is safer to use and is to be preferred. Liquid oxygen is more easily available and can also be prepared at the site with liquid nitrogen. For field operations, liquid nitrogen should be carried and liquid oxygen prepared as needed on site.

Desorption from glass beads for all HCs of interest is accomplished by heating the freezeout trap with boiling water for 3 minutes or by electrical heating at 90°C. The sample is transferred into the GC-FID unit by the carrier gas itself. Figure 5 shows the sampling and injection modes of a preconcentration trap.



(a) FILL POSITION



(b) INJECTION POSITION

Figure 5. A schematic diagram of sample preconcentration and injection steps.

The simplest procedure for measuring the volume of air sampled is by installing a 2-liter stainless steel canister at the freezeout trap exit. This canister can be the same as the sampling canisters but its volume must be accurately determined. The actual volume sampled can be calculated by carefully monitoring the pressure change in this canister. Figure 5 shows the specifications of one recommended vacuum and compound range pressure gauge. This 8-1/2 inch diameter precision gauge (Wallace and Tiernan, Inc., Belleville, New Jersey) is available in the -380 to +380 mm Hg pressure range and has an accuracy of ±0.4 mm Hg and a sensitivity of ±0.06 mm Hg. Typically, when the sampling canisters are at 30 to 40 psig pressure, the vacuum part of the gauge is not necessary. In a 2-liter vessel a pressure change of 190 mm Hg (at a 760 mm Hg total pressure) would correspond to a 500 ml sample volume. When the sample canister is poorly pressurized (5 to 10 psig) it may be desirable to operate the volume monitoring canister at a slight vacuum. This would ensure smooth flow through the freezeout trap.

While an accurate volume of the injection air sample is essential, the volume need not be the same all the time. An overall sampling accuracy of better than ± 3 percent is attainable. Note, however, that neglect of water vapor in air can cause an error of ±0 to 2 percent. For determining air quality, this is not significant.

To perform an actual transfer operation refer to Figure 5. Valve A is closed and valves B and C opened to ensure a leak-proof system as indicated by pressure gauge PG1. If so, valves A and D can now be opened. The freezeout loop should be immersed in hot water and purged with the sample to flush out the system for 20 seconds. Valves B and D should now be closed and the pressure on gauge PG2 read carefully. The hot water should now be replaced with liquid oxygen (or argon) and valve B quickly opened. The sampling valve should be changed to the inject position and liquid oxygen quickly replaced with hot water for 3 minutes. At the end of the sampling period final pressure on PG2 should be noted and valve B closed. It should be added that the final pressure on PG2 can be predetermined once a sample size has been established. The actual sample volume preconcentrated can be calculated as follows:

$$\Delta V = \text{volume sampled} = \frac{V_1 \cdot 298}{P_s \cdot (t + 273)} \Delta PG2$$

where ΔV is the volume sampled at standard atmospheric pressure P_s (760 mm Hg) and temperature (25°C), ΔPG2 is the pressure change on gauge PG2, V_1 is the vessel volume, and t is the sample temperature.

C. *Chromatographic Separations and Analyses of HC Species Data*

In the previous section the procedures for collection and preconcentration of a known volume of air on a freezeout trap were defined. The trace chemicals are thermally desorbed and directly injected into the GC. Details of column packings and other procedures that must be followed to obtain HC species data shall be provided here.

Dividing HC species into two major groups, light hydrocarbons (C_2-C_6) and heavy hydrocarbons (C_6-C_{12} HCs), is feasible. Some duplication occurs in the C_2-C_6 analysis and C_6-C_{12}

analysis. This redundancy is a good internal check on the reliability of the two methods. Methane (CH_4) plays an unimportant role in photochemical O_3 generation in polluted atmosphere and is not considered to be a hydrocarbon of interest here. Methane is not collected on the freezeout traps under the preconcentrating conditions recommended here.

1. *Light Hydrocarbon Species (C_2-C_6 HCs)*

Light HC species are easily measured by injecting a 500-ml sample of air into a GC-FID micropacked column system. Table 8 summarizes the GC conditions that are recommended for C_2-C_6 HC species analysis. Column No. 1 is recommended primarily because it allows isothermal operation and greatly simplifies the analysis of light HCs. Column 1, however, cannot be heated above 60°C and all column preconditioning should be done at 50°C. Column No. 2 is an equally reliable column but temperature programming is absolutely essential. Subambient temperature programming is used on Column 2 and hence this operation is more tedious. Figures 6 and 7 shows chromatograms of C_2-C_6 HC species analysis with the recommended Column 1. No two columns are exactly identical. For example, Figure 6 and 7, although obtained from nearly identical GC columns, do not produce identical chromatograms. Each column should be tested and optimized for best possible operation at each laboratory. The excellent performance of Column 2 with subambient temperature programming is also demonstrated in Figure 8. The simplicity of the operation of Column 1 makes it highly preferable. Generally, Column 1 should not be used after hexane has been resolved. As will become clear, 2-methylpentane, hexane etc. are also resolved during heavy hydrocarbon species analysis. This overlap provides a good internal check on the reliability of two columns.

2. *Heavy Hydrocarbons (C_6-C_{12} HCs)*

Because of the complexity of the C_6-C_{12} HC mix in ambient air, it is essential to use capillary columns. Three major advantages compared to non-capillary columns are realized:

- Analysis of all C_6-C_{12} HCs is accomplished in a single operation.
- Higher resolution for the same analysis time or equal or better resolution in much less time is obtained.
- Higher sensitivity.

In the past, for example, C_5-C_{10} aliphatics and aromatics required at least two GC columns for effective separation (Lonneman et al., 1974). The complexity of C_5-C_{12} HCs is ideally resolved and quantified with the help of high resolution capillary columns. However, capillary columns suffer from a lower operational life and require careful handling when compared to packed columns. The advantages of capillary columns far outweigh their disadvantages. For the analysis of higher than C_6 HCs, Columns 3 and 4 (Table 8) are recommended. Although the dimensions are different, Columns 3 and 4 are both SE-30 glass capillary columns and therefore very similar. Both columns can resolve major C_5-C_{12} HCs satisfactorily, although Column 3 operation is expected to give superior resolution. While temperature programming is essential for both Columns 3 and 4 operations, the former operation requires subambient temperature programming (-30°C to 80°C). As discussed in subsequent paragraphs, Column 3 operation is superior and is recommended when possible. Column 4 operation is clearly simpler (above ambient temperature programming) and also acceptable.

TABLE 8. GC COLUMN SELECTION AND OPERATING CONDITIONS FOR DETAILED HC SPECIES ANALYSIS

Category	Column No.	Column Description	Operation	Total Time per Sample (minutes)	Typical Sample Size (ml)	Detector		Typical Carrier Flow Rate (ml/min)	Remarks
						Type	Temp. (°C)		
Light Hydrocarbons (C_2-C_6 HCs)	1	5m x 1/16-in. i.d., Ni, Durapack Phenyl-isocyanate/Porasil C, 100/120 mesh (micropacked)	Isothermal operation at 40°C	40	500*	FID†	250	30	Recommended column. Requires no temperature programming. Maximum column temperature = 60°C. Column conditioning to be done at 50°C. Low bleed. Good operation at all relative humidities.
	2	6 m x 1/16-in. i.d., SS, Durapack n-octane/Porasil C, 100/120 mesh	Programmed temperature operation necessary -70°C to 65°C at 15°C/min-hold at 65°C for 25 min.	40	500*	FID	250	5–10	Without temperature programming either C_2H_6/C_2H_4 or C_2H_2/C_3H_8 cannot be resolved. Maximum column temperature is 175°C. Column conditioning to be done at 150°C. Low bleed. Good operation at all relative humidities.
Heavy Hydrocarbons (C_6-C_{12} HCs)	3	30m SE-30 glass capillary, 0.25-mm i.d., W.C.O.T.	-30°C for 8 min, -30°C to 80°C at 4°C/min, 15 min at 80°C	60	300–500*	FID	250	1–2	Column 3 when used under prescribed conditions is recommended for high quality data collection. Subambient temperature programming is essential. Good operation occurs at all relative humidities. SE-30 is to be preferred over OV-101, which has been traditionally used and suffers from bleed and artifact problems.
	4	50m SE-30 glass capillary, 0.5-mm i.d., W.C.O.T.	45°C for 8 min, 45 to 150°C at 8°C/min, 10 min at 150°C	60	300–500*	FID	250	1–2	Column 4 is very similar to Column 3. Because of programming at above ambient temperatures the peak shapes may be inferior. Column 4 usage is acceptable if subambient operation is to be avoided.
Tracer	4	2m x 1/8 in, 10% DC-200 on 80/100 mesh carbowax W (A/W) plus 3 in. x 1/8 in. Ascarite trap	Isothermal operation at 45°C	20	5	ECD†	250	40	A single tracer such as CCl_3F (F11) is acceptable. F11 is measured in 5 min, but other chlorinated species are expected. Ascarite trap is used to remove water. Measurement of a tracer during HC species analysis is optional but usually quite valuable.

*Collected on a 4 x 1/8 in. 80/100 mesh glass head trap at liquid O_2 (or liquid Ar) temperature

†FID-Flame Ionization Detector; ECD-Electron Capture Detector.

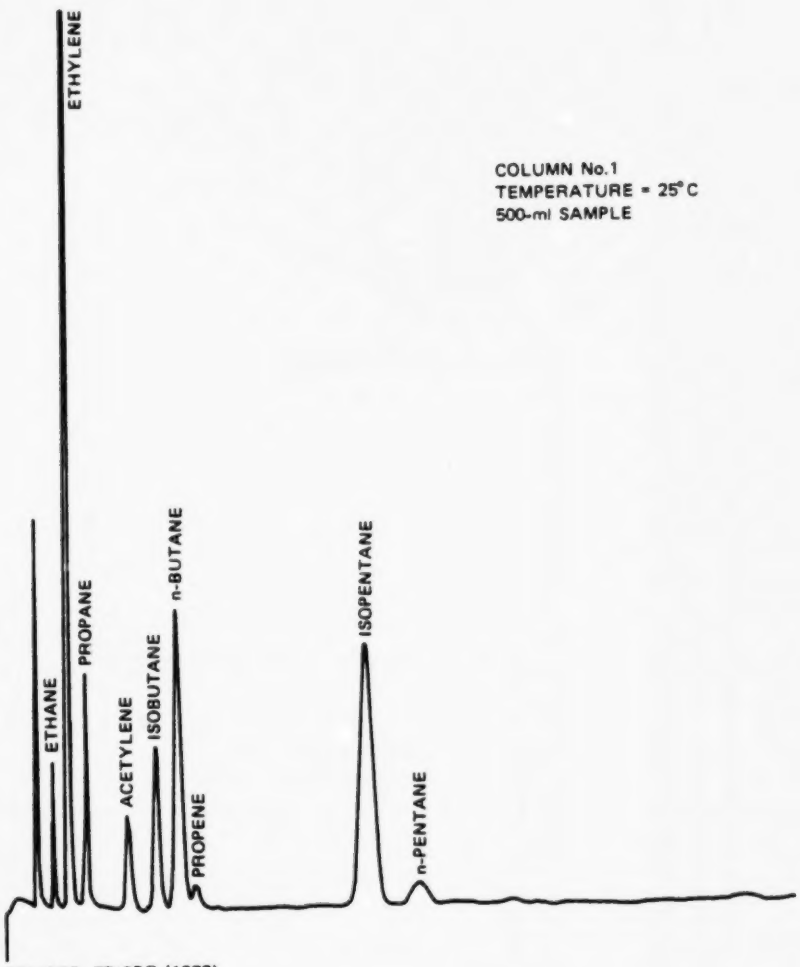


Figure 6. Light HC (C_2-C_6) analysis in rural air.

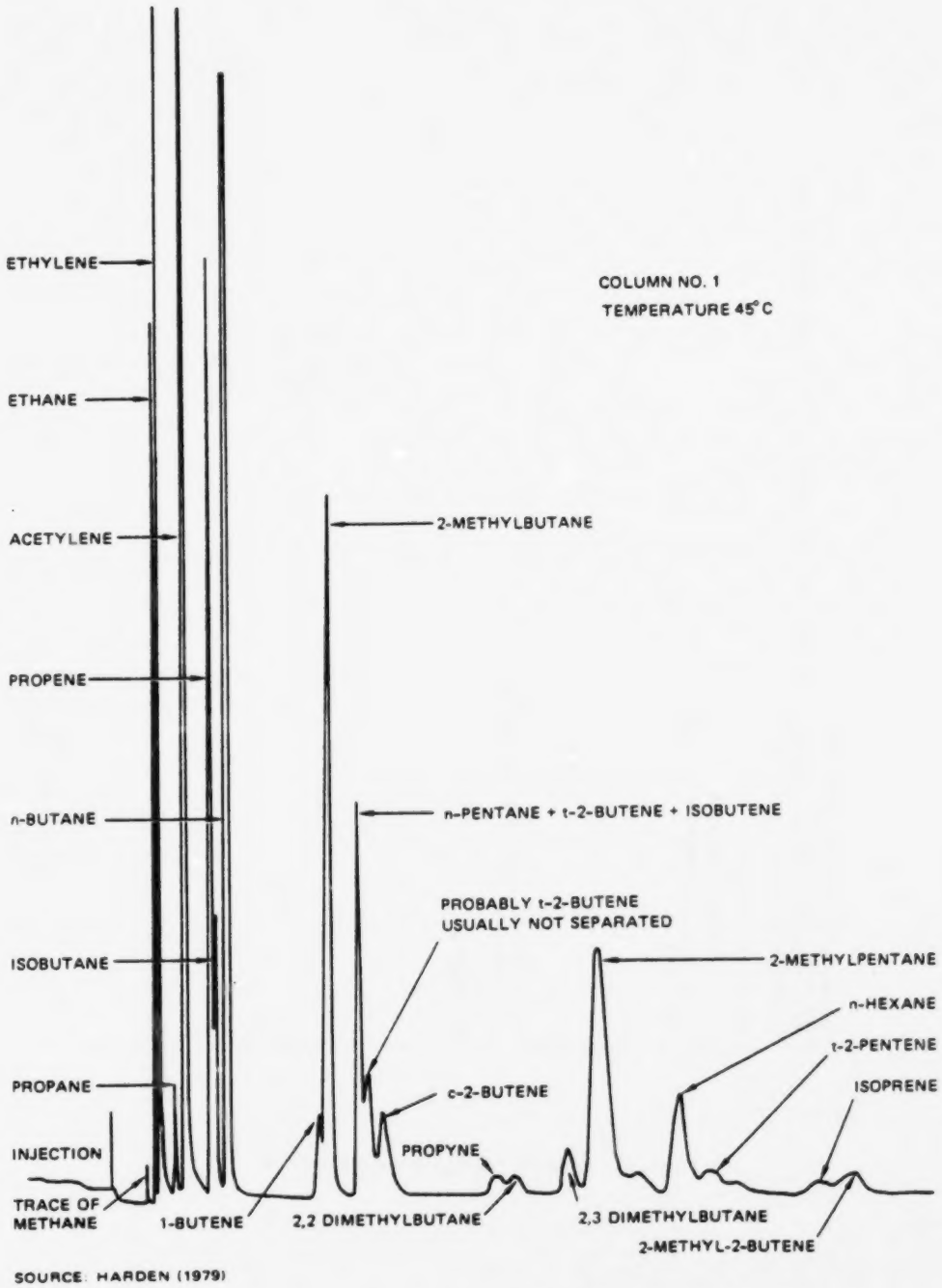
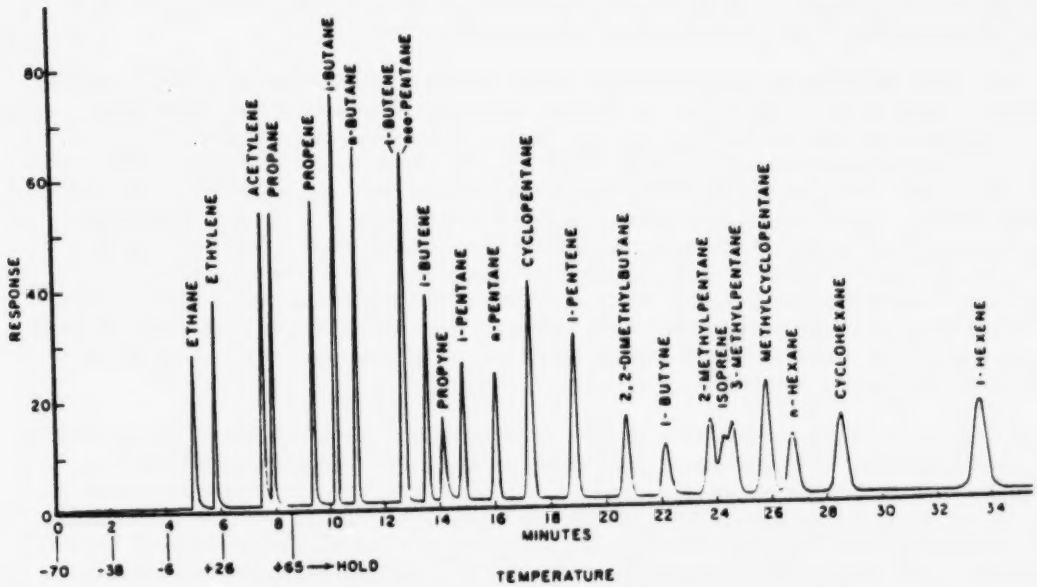
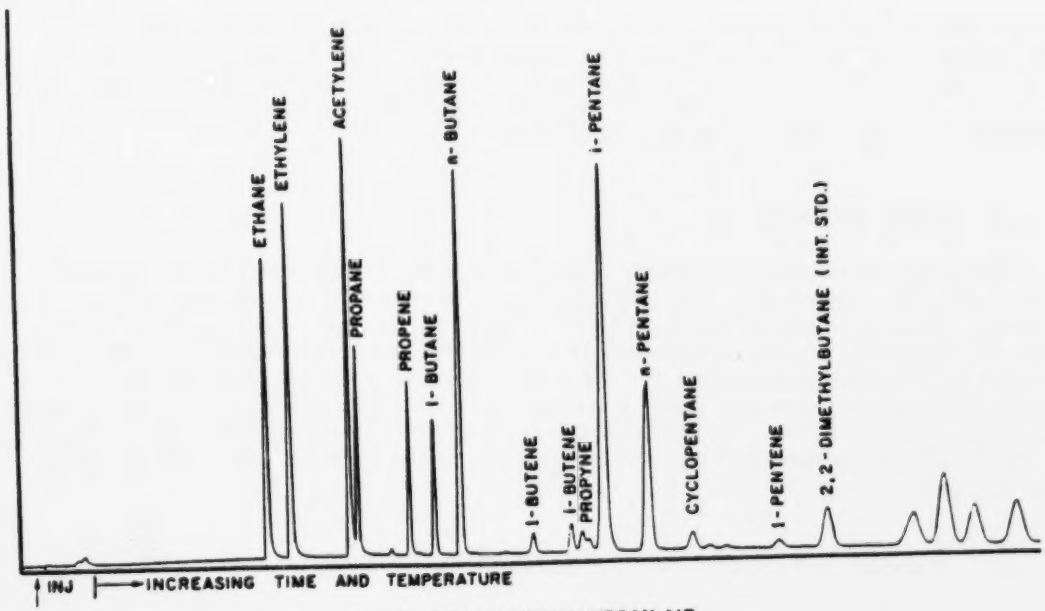


Figure 7. C_2-C_6 HC species analysis of an auto exhaust air sample



(a) COLUMN 2: STANDARD GAS MIXTURE — -70 TO 65°C, 16°/min



(b) COLUMN 2: PHOENIX URBAN AIR

SOURCE: WESTBERG et al. (1974)

Figure 8. Typical ambient air chromatogram showing resolution of C_2-C_5 hydrocarbon fraction.

Subambient GC operations add an additional complexity that in itself is neither difficult nor problematic, however. In reality, once initiated subambient GC operation is quite routine and at the very least allows a greater range of temperature programming.

The carrier flow rate through a capillary column is only 1 to 2 ml/min, and this is used to flush the trapped sample into the GC. In Column 3 operation, because of the subambient column temperature (-30°C), the trace HCs are trapped at the head of the column and then released during temperature programming of the GC oven. This results in sharper peaks and better resolution. Chromatograms in Figures 9 (also Table 9) and 10 (also Table 10) show the resolution of C_6-C_{10} HCs on capillary Columns 3 and 4, respectively. A greater number of peaks are shown to be well resolved in Figure 9. Most of the important peaks are also relatively well resolved in Figure 10 where subambient temperature is not used. Considering that 10 to 35 percent of the NMHC burden is currently unidentified; both Column 3 and Column 4 operations are considered acceptable. In the future, as more of the similar peaks are identified, Column 3 operation would be clearly preferable. Note that in both Figures 9 and 10 the GCs show excellent baseline stability.

In both cases, however, only HCs up to C_{10} are identified. (Note that not all HCs up to C_{10} have been identified.) This HC fraction constitutes a major part of the ambient HC burden. However, Columns 3 and 4 would also measure HCs greater than C_{10} but these are not routinely found to be present in large amounts. Similarly, natural terpenoid HCs are also resolved on Columns 3 and 4 (Table 8) (at the very end of the Figure 9 and 10 chromatograms), but are not generally found in significant quantities. HCs above C_{10} would be resolved and measured on Columns 3 and 4, but would be part of the "unknowns." Typically, however, HCs greater than C_{10} would form a very small fraction of the NMHC as well as of the overall "unknown" fraction.

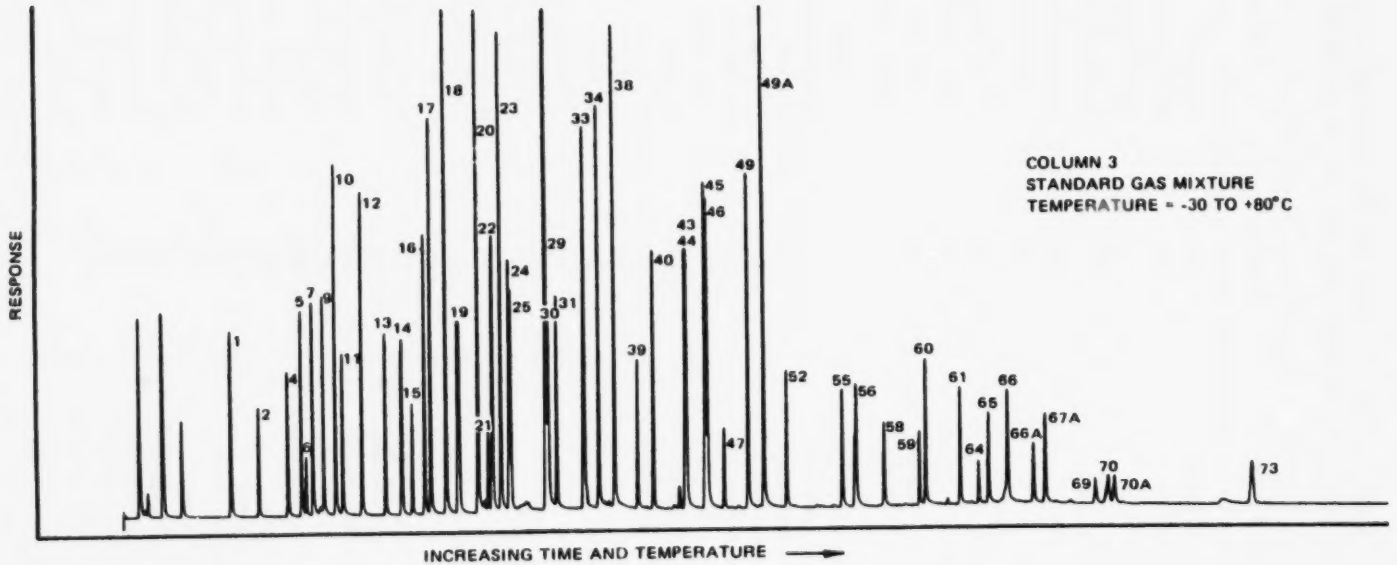
As demonstrated in Figure 11, at early stages of HC resolutions on Columns 3 and 4, the chromatograms of ambient air mixtures are highly complex. Often it is desirable to measure some species (such as 2-methylpentane or hexane) on both columns for internal checks. Thus C_2-C_6 HCs up to (or including) 2-methylpentane are measured on Column 1 and C_6-C_{12} HCs after (or including) 2-methylpentane on Column 3 or 4.

3. *NMHC Measurements*

For many applications (such as the EKMA model), the only input required is total NMHCs (6 to 9 am) and therefore separation and identification of individual species need not be stressed. The only reason for conducting detailed species analysis in such instances arises from the unreliability of continuous NMHC measuring instruments at concentrations below 0.5-1.0 ppm C. In that case, Columns 1 and 4 are recommended. A 2-methylpentane cutoff can be used in both columns. Thus, all peaks to 2-methylpentane can be added up on Columns 1 and the remainder of Column 4. The individual Column 1 and 4 responses can then be converted to the concentrations (based on carbon response) and added to obtain total NMHC concentration (e.g., ppb C).

4. *Aldehydes and Other Oxygenated Species*

While oxygenated species are expected to constitute only a small fraction (<5 percent) of the total NMHC burden, these species (especially aldehydes) can make a disproportionately large contribution to photochemical smog formation. Unfortunately, no reliable instrumental measurement method is currently available.



NOTE: For peak identification refer to Table 9.

SOURCE: WESTBERG (1979)

Figure 9. Chromatogram showing resolution of a standard mixture of C_5-C_{10} hydrocarbons on SE-30 glass capillary column with subambient temperature programming.

TABLE 9. STANDARD GAS MIXTURE MEASURED ON SE-30 CAPILLARY COLUMN WITH SUBAMBIENT TEMPERATURE PROGRAMING

Peak No.*	Chemical Name	Peak No.*	Chemical Name
1.	2-Methyl-1-butene	39.	n-Heptane
2.	2-Methylbutane	40.	Methylcyclohexane
3.	Halocarbon	41.	Trimethylcyclopentane
4.	1-Pentene	42.	Ethylcyclopentane
5.	3-Methyl-1-butene	43.	2,5-Dimethylhexane
6.	n-Pentane	44.	2,4-Dimethylhexane
7.	Isoprene	45.	2,3,4-Trimethylpentane
8.	Carbon disulfide	46.	Toluene
9.	t-2-Pentene	47.	2,3-Dimethylhexane
10.	c-2-Pentene	48.	2-Methylheptane
11.	2-Methyl-2-butene	49.	3-Ethylhexane
12.	2,2-Dimethylbutane		3-Methylheptane
13.	Cyclopentene	49A.	2,2,5-Trimethylhexane
14.	Cyclopentane	50.	C-9 Alkane
	4-Methyl-1-pentene	51.	Dimethylcyclohexane
15.	2,3-Dimethylbutane	52.	n-Octane
16.	2-Methylpentane	53.	Ethylcyclohexane
	t-4-Methyl-2-pentene	54.	C-9 Alkane
17.	c-4-Methyl-2-pentene	55.	Ethylbenzene
18.	3-Methylpentane	56.	p-Xylene
19.	2-Methyl-1-pentene		m-Xylene
	1-Hexene	57.	Styrene
20.	n-Hexane	58.	o-Xylene
21.	t-2-Hexene	59.	n-Nonane
22.	2-Methyl-2-pentene	60.	i-Propylbenzene
	t-3-Methyl-2-pentene	61.	n-Propylbenzene
23.	c-2-Hexene	62.	3-Ethyltoluene
24.	Methylcyclopentane	63.	2-Ethyltoluene
25.	c-3-Methyl-2-pentene	64.	1,3,5-Trimethylbenzene
26.	2,2,3-Trimethylbutane	65.	1-Ethyltoluene
27.	1,1,1-Trichloroethane	66.	1,2,4-Trimethylbenzene
28.	2,4-Dimethylpentane	66A.	sec-Butylbenzene
29.	Benzene	67.	1,2,3-Trimethylbenzene
30.	1-Methylcyclopentene	67A.	n-Decane
31.	Cyclohexane	68.	Methylstyrene
32.	2-Methylhexane	69.	1,3-Diethylbenzene
33.	2,3-Dimethylpentane	70.	1,4-Diethylbenzene
34.	3-Methylhexane	70A.	1,2-Diethylbenzene
35.	Dimethylcyclopentane	71.	C-10 Substituted benzene
36.	Dimethylcyclopentane	72.	C-10 Substituted benzene
37.	Dimethylcyclopentane	73.	Undecane
38.	2,2,4-Trimethylpentane		

*Key to Figures 9 and 11.

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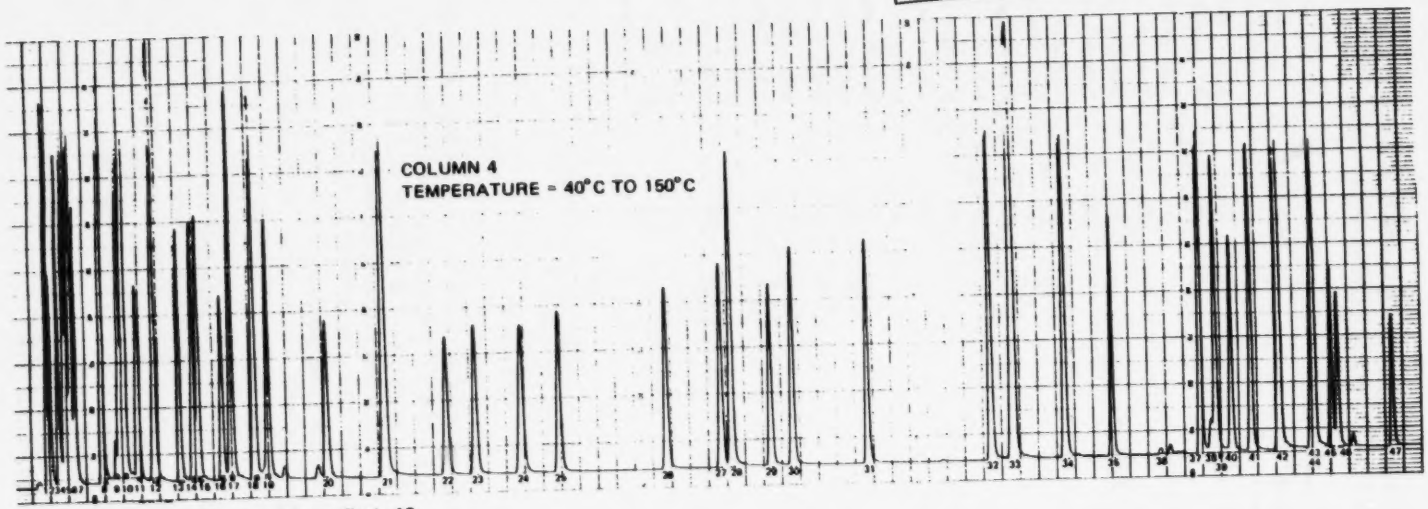


NOTE: For peak identification refer to Table 10.

SOURCE: HARDEN (1979)

Figure 10. Chromatogram showing resolution of a standard mixture of C_5-C_{10} hydrocarbons on SE-30 glass capillary column with above ambient temperature programming.

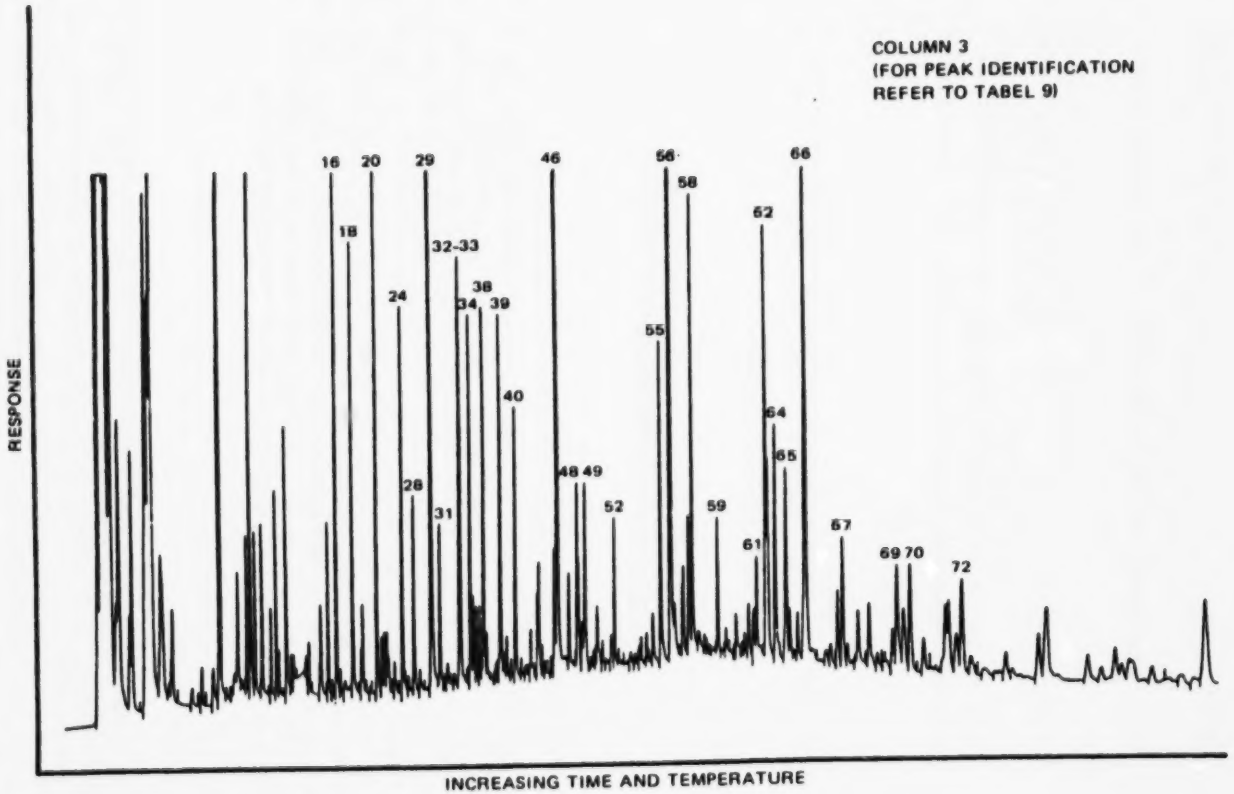
TABLE 10. STANDARD GAS MIXTURE MEASURED ON SE-30 GLASS CAPILLARY COLUMN WITH ABOVE AMBIENT TEMPERATURE PROGRAMMING

Peak No.*	Chemical Name	Peak No.*	Chemical Name
1.	Propane + Propene	25.	2,2,4-Trimethylpentane
2.	Propyne	26.	2,5-Dimethylhexane
3.	Isobutane + 1-Butene	27.	2,3,4-Trimethylpentane
4.	——	28.	Toluene
5.	Cis-2-butene + 2,2-dimethylpentane	29.	2-Methylheptane
6.	1,4-Pentadiene	30.	3-Methylheptane
7.	2-Methylbutane	31.	n-Octane
8.	Isoprene	32.	Ethylbenzene
9.	n-Pentane	33.	p/m Xylene
10.	t-2-Pentene	34.	o-Xylene
11.	2-Methyl-2-butene	35.	n-Nonane
12.	2,2-Dimethylbutane	36.	Alpha Pinene
13.	4-Methyl-1-pentene	37.	n-Propylbenzene
14.	2,3-Dimethylbutane	38.	Beta Pinene
15.	2-Methylpentane	39.	m-Ethyl toluene
16.	3-Methylpentane	40.	1,3,5-Trimethylbenzene
17.	2-Methyl-1-pentene	41.	o-Ethyltoluene
18.	n-Hexane	42.	1,2,4-Trimethylbenzene
19.	1-Hexene	43.	s-Butylbenzene
20.	2,4-Dimethylpentane	44.	n-Decane
21.	Benzene	45.	1,2,3-Trimethylbenzene
22.	2-Methylhexane	46.	Limonene
23.	3-Methylhexane	47.	n-Butylbenzene
24.	n-Heptane		

*Key to Figure 10.

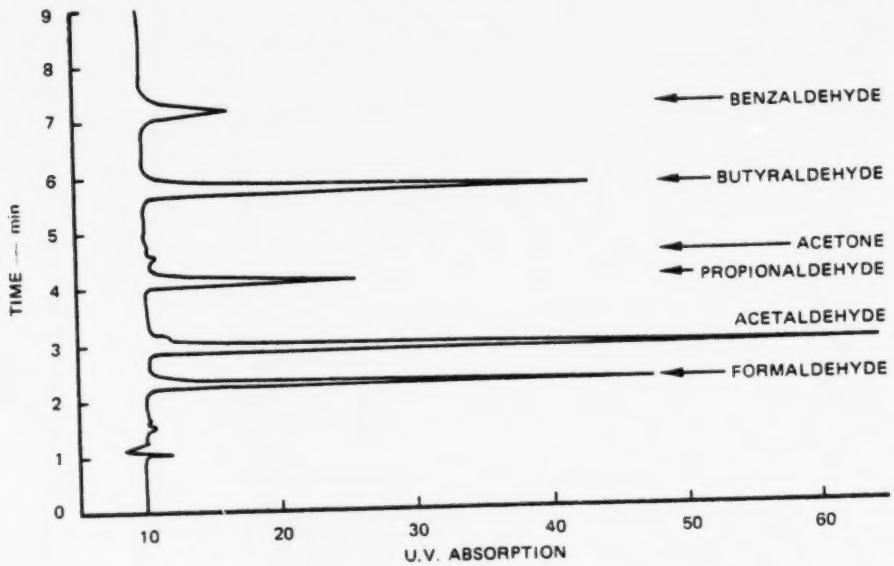
In the interim, wet chemical methods may be used to measure total aliphatic aldehydes. These involve changes in the color of a chemical solution whose absorbance is measured with a spectophotometer and compared with standards. A sensitivity of 1 ppb is possible, but many potential interferences exist. Total water soluble aliphatic aldehydes are measured as formaldehyde in ambient air. A 10-ml volume of 0.05 percent MBTH (3-methyl-2-benzo thiazolone hydrazone hydrochloride) is used as a collecting medium. Aliphatic aldehydes react with MBTH in the presence of ferric chloride to form a blue dye in acidic media (U.S. Public Health Service, 1965; Joshi, 1978). A 100-liter air sample is necessary to obtain a 1 ppb sensitivity.

Several promising procedures are being actively developed. One of these methods (Grosjean, 1979) entails sampling of large volumes of air on dinitrophenylhydrazine cartridges and analysis by high performance liquid chromatography (HPLC). The method could potentially measure less than 1 ppb of aliphatic and aromatic aldehydes. Figure 12 shows the separation of a synthetic mixture of hydrazones of aldehydes. The method, however, has yet to be field tested.



SOURCE: HOLDREN, et al. (1979)

Figure 11. Chromatogram of ambient air (500 ml) samples directly from a stainless-steel container.



SOURCE: Grosjean (1979)

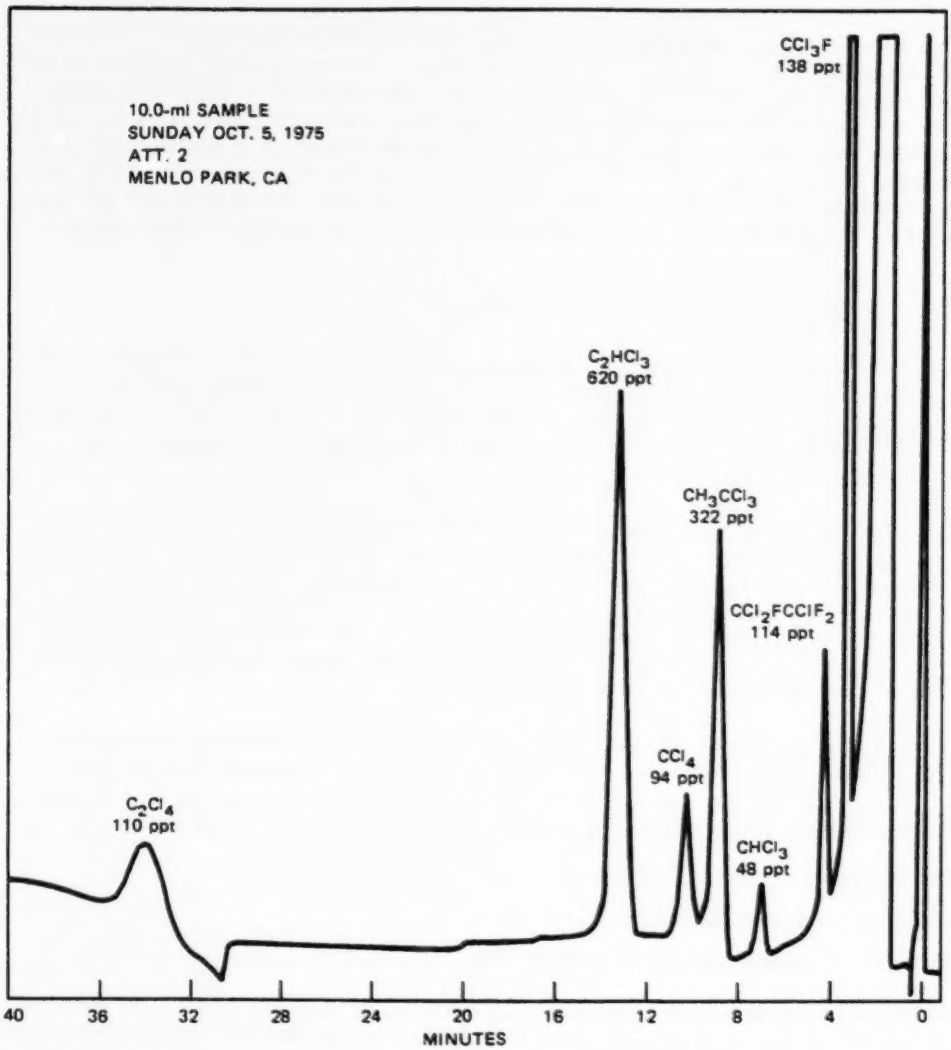
Figure 12. HPLC-UV separation of a synthetic mixture of hydrazones of C_1-C_4 aliphatic aldehydes, benzaldehyde, and acetone.

5. *Atmospheric Tracers*

Typically, the analysis of one inert tracer serves as a useful indicator of the degree of urban contamination. The analysis of fluorocarbon-11 (CCl_3F) is recommended. It is one of the most inert chemicals in the environment and is easily measured. A 5-ml direct injection of air into a GC-EC system with a 2 m DC-200 column (see Table 8) is adequate for the analysis of CCl_3F Figure 13 shows a chromatogram of CCl_3F separation from ambient air. A standard permeation tube can be used to establish the CCl_3F concentration in a secondary standard (Singh et al., 1979). In the canisters recommended here for sampling, CCl_3F is stable for a period of several years. One canister could be set aside as a secondary standard for CCl_3F analysis. Such tracers (along with HC tracers such as C_2H_2) can often provide useful information about the nature of the HC mix but do not themselves contribute to photochemical smog.

D. *Routine Identification of HCs*

Extensive past research has led to the identification of a large number of ambient HCs, mostly with the help of GC/MS techniques. For routine analysis, retention time can be used as a reliable identifier of GC peaks. As is clear from Figures 9 and 10, retention times must be carefully determined and labelled if GC peaks eluting close to each other are not to be confused. Most of the unknown HC species are typically those present in small amounts. Therefore, direct identification and measurement of only the major species that collectively form a significant fraction (65-90 percent) of NMHCs is possible at this time.



SOURCE: SINGH et al (1979)

Figure 13. Ambient air chromatogram showing resolution of Fluorocarbon-11 and other halocarbons.

A computerized data system is mandatory when utilizing capillary columns. The operator should always possess a well-identified marking system containing a list of HCs such as shown in Table 9. The retention times of individual peaks must be known. For day-to-day operation, a standard spectrum is extremely useful in assigning the correct chemical name to the peaks based on retention times. A number of data systems available in the market (e.g., Hewlett Packard, Perkin Elmer, Spectra Physics), plot the chromatogram and mark the exact retention time. Relative retention times based on one or more well-characterized species (e.g., benzene or toluene) are calculated and corresponding peaks identified.

Such a process should not be fully automated. Manual checks of measured chromatograms with that of the standard should be made frequently. In practice, both retention times and relative retention times can be reproduced with extreme precision. However, an experienced operator can visually recognize the major peaks and chances of mislabeling a peak are greatly reduced. Automatic identification (based on retention times) using available data systems is feasible. For the analysis of C_6-C_{12} HCs, however, we strongly recommend that manual visual identifications also be made to reduce any chances of error. These problems are much less severe for C_2-C_6 HC analysis, largely because of the smaller number of chemical species.

E. *Primary Standards and NMHC Species Calibrations*

The uniform carbon response of an FID can be used for the calibration of NMHCs with an accuracy of ±5 to ±8 percent* (Lonneman, 1979). This error is quite reasonable when one considers that primary standards with an accuracy of much better than ±5 percent are rarely available. Thus, calibrations carried out with a select group of HCs can be used for the quantification of all NMHC species.

The single most desired standard is the traceable National Bureau of Standards (NBS) propane standard. Best NBS estimates suggest that the mean concentration of the NBS propane standard is within ±2 percent (95 percent confidence limit) of the specified value. NBS propane standards in air are available in concentrations of 1 ppm, 3 ppm, 10 ppm, 50 ppm, 100 ppm and 500 ppm. Standards are stored in high-pressure stainless steel cylinders. Propane is stable over a period of at least 1 year. All standards, whether internally generated or externally obtained, must be referred to the NBS propane standard.

At SRI a 5-ppm mixture of benzene and toluene in high-pressure aluminum cylinders (Scott-Marrin, Riverside, California) has remained unchanged (±3 percent) over a 1-year period. It is recommended that any laboratory conducting HC species analysis should possess the following standards (preferably in 5-ppm concentrations) for NMHC analysis:

- NBS propane standard in air (STD1)
- Propane + hexane standard in air (STD2)
- Benzene + toluene standards in air (STD3).

All of these are commercially obtained. Most commercial suppliers refer to the NBS propane standard (STD1), but each laboratory must verify the concentration(s) independently. The NBS propane standard can be directly used for the calibration of C_2-C_6 HCs. However, STD2 is recommended as a duplicate. STD2 can also be used for C_6-C_{12} HC species analysis. Hexane offers a clear advantage because it is conveniently analyzed on columns for light as well as heavy HC species analysis. Benzene and toluene standard (STD3) is an independent check on the C_6-C_{12} HC species carbon response.

The 10^6 linear dynamic range of the FID ensures a linear response over the entire low-ppm to low-ppb concentration range. This, however, should be routinely tested. Standards

*This is generally not true of HCs containing oxygen (oxygenated species) and chlorine atoms (fluorocarbons, etc.).

should always be stored at ppm concentration levels. Any dilutions can be a single step operation and should be conducted on the day of detailed calibrations. FID response has been found to be unchanged over a period of many months. A single standard, however, must be used frequently to confirm the proper operation of the FID system. Detailed calibrations and multiconcentration levels should be conducted at least once a week. More frequent calibrations may be warranted if the FID response is found to change, but this should not occur under normal operating conditions.

F. *Archiving HC Data*

If only a few ambient air samples are analyzed for HC species, the data can be written on individual sample sheets and examined by simple inspection. If many air samples are analyzed, on the other hand, particularly over a time period which may be measured in years, such a data storage system is clearly unsatisfactory. The data must be stored on cards or magnetic tape.

Several years ago, EPA developed AEROS (Aerometric and Emissions Reporting System) for the purpose of archiving aerometric and emissions data. The sub-system developed for storing pollutant data is SAROAD (Storage and Retrieval of Aerometric Data). SAROAD works well for the criteria pollutants such as SO_2, O_3, NO_2, etc.; but, while the sub-system can be made to accept HC species data from ambient air samples, it is very awkward to do so. Retrieving HC species data from AEROS for analysis is particularly tedious and time-consuming. Because of this, very little of the HC species data from past studies can be found in AEROS. Instead, the data are stored on sample data sheets, or in project reports, and therefore have been incompletely analyzed.

An alternative storage system has been devised recently (Nitz and Martinez, 1980) which shows promise of minimizing some of the problems associated with archiving HC species data. The new system stores the data by assigning a number to each identified (or unknown) HC species in a sample, which itself is uniquely identified by sampling time and location. Simple software can be written to analyze the data from many samples. EPA is storing HC data from its summer studies using this system, and plans to do so in the future. It is recommended that State and local agencies give serious consideration to storing their data in this manner also.

SECTION 7

QUALITY CONTROL (QC) AND QUALITY ASSURANCE (QA)

Because of the complexity of the ambient air mixture and the relative sophistication of analytical techniques, a great number of pitfalls are possible. Because of the expense and effort involved, it is essential to ensure that the collected HC species data meet stringent requirements. Detailed QC and QA procedures should be developed after the program designs (including equipment and operational procedures) have been decided. Many of the special precautions and procedures are addressed in this report. This section describes a sample protocol to serve as an example.

Certain areas of the operational procedures lend themselves to systematic checks to achieve high quality data. These areas are as follows:

- Sample collection
- Sample preconcentration
- Calibration standards
- Calibration of gas chromatograph response
- Verification of gas chromatograph linearity
- Data collection reporting and HC identification
- Referee samples for interlab comparison.

Sample Collection—Loss of data quality due to the sample collection process is usually attributable to chemical loss on the surfaces of the pressurizing pump, tubing, or sample canisters as well as outgassing of species from sampling lines. Samples must be collected by means of a noncontaminating pump (stainless steel bellows pump such as the MB 158) and 2-liter containers fabricated from electropolished (passivated) stainless steel. Sample canisters should be baked (100°C) and flushed with zero air before use to remove any HCs present as a result of the manufacturing process. Ultrapure air should be analyzed before and after sampling to ensure cleanliness of the entire sampling protocol. The same procedure should be repeated with a complex HC mixture to ascertain the absence of surface removal problems. Three sample canisters or 10 percent of the inventory of canisters, whichever is greater, should be checked to verify storage stability of ambient air. This air, after storage of 1 week in the sample canister, should exhibit a combined HC concentration within ± 5 percent of that at the start. Ambient sample storage in stainless steel canisters should be limited to 1 week prior to analysis. Samples are collected in duplicate and all collected samples must be analyzed.

Sample Preconcentration—Errors in HC measurements are sometimes attributable to the preconcentration system, or, with far less likelihood, sample loss on the media used for cryogenic preconcentration. Leak checks should be conducted on the preconcentration system routinely or whenever calibration information indicates an instrumental change or malfunction.

Loss of sample during preconcentration can be verified by comparing instrument response to calibration standards with the preconcentration system bypassed and in-line. A daily standards check will be helpful in the identification of these problems.

Calibration Standards—Potential measurement errors can occur due to changes in the HC concentration in multicomponent mixtures contained in compressed gas cylinders. Compressed gas standards are used to calibrate instrument response to specific HCs, to calibrate flame detector linearity, and to evaluate system sample loss. System sample loss may be caused by leaks within the plumbing by adsorption or reaction of the sample with the internal surfaces of the system. Two types of calibration standards can be employed. First, two compressed gas working standards containing a mixture of propane/hexane and benzene/toluene in air in individual anodized aluminum cylinders at a nominal concentration of 5 ppm, can be used. Second, a standard compressed gas cylinder containing propane at a 5 ppm concentration certified by the NBS shall be used as the reference standard. The NBS propane standard should be used as a primary standard within the period of certification (about 1 year) and will serve as a reference to evaluate the concentration and the stability of the multicomponent working standard.

Calibration of Gas Chromatograph Response—Calibration of instrument response by injection of the multicomponent working standard should be performed after every fifth ambient sample, or twice per day, whichever is more frequent. The precision of the single point calibration should be ±5 percent or better. If the precision of the calibration is not within ±5 percent, then the system should be recalibrated, checked for leaks, and appropriate trouble shooting procedures applied. Calibration of gas chromatograph linearity is also recommended whenever the precision of the single point calibration deviates by more than 5 percent from previous calibration.

Calibration of Gas Chromatograph Linearity—The linearity of the gas chromatograph should be verified once each week of operation. A diluted gas standard is prepared using an evacuated 1 to 5 liter stainless steel canister. A known volume of working calibration standard is injected through a diaphragm (or with a syringe) into the canister and the canister is pressured, by zero air, to 40 psig. A 100 to 200 ppb concentration standard should be prepared in this way. A series of sample loops from 50 ml to 1 ml (or cryogenic trapping of 10 to 100 ml volumes) are used to obtain instrument response with at least five HC concentrations. When sample size versus instrument response is plotted, the results should fall along a straight line.

Data Collection, Reporting and HC Identification—The reports should contain records of gas chromatograph response to single point calibration standards and to multipoint calibrations for instrument linearity. The results of ambient sample analysis should contain tabulations of HC identification (if known), elution time, and gas chromatograph response. Samples of important HCs on the urban atmosphere list should be obtained and used to verify elution time during analysis on the equipment of interest.

Reference Samples for Interlab Comparison—All samples should be collected and analyzed in duplicate. A total of 5 percent of the ambient HC samples collected will be used for interlaboratory comparison. Specific details as to distribution of referee samples will be developed within the HC measurement program. A maximum delay from collection to analysis may not exceed 1 week. The referee sample processing will provide independent audit of each laboratory's analytical procedures.

SECTION 8

RECOMMENDED MEANS FOR OBTAINING HC SPECIES DATA

Samples of ambient air are collected on selected days in summer months for analysis of their NMHC concentrations. It is recommended that such data could be most efficiently acquired by outside contractual procurements. In-house capabilities should be considered but the expense involved in acquiring sophisticated instrumentation as well as the difficulties involved in effective use of personnel with dedicated expertise in HC species analysis makes this an expensive option. Outside contractors can bring together single or multi-institutional experience and are available when needed. This makes it highly cost-effective. Hence the use of outside contractors is recommended.

Currently, the number of outside contractors that could handle future needs of state and local agencies are somewhat limited and generally tend to be research-oriented organizations. State and local organizations should obtain guidance from their regional offices for suggestions regarding the suitability of private contractors.

Cost of analysis is highly variable and depends upon the number of samples to be analyzed. For detailed C_2-C_{12} HC species the average cost can be expected to range between 150-300 dollars per sample.

SECTION 9

KNOWLEDGE GAPS AND RECOMMENDATIONS

Several recommendations became evident during the conduct of this study. These arise because HC species identification and measurement procedures are still deficient and need to be further improved. These improvements are likely to increase the complexity as well as the expense of analysis. Alternate methodologies that simplify these complex procedures should therefore be vigorously pursued. The following specific recommendations are proposed:

- Continuous NMHC analyzers provide an inexpensive and routine means of HC data collection. At this time, there is no clear concentration cutoff above which these become acceptable, although 1 ppm C is commonly assumed. If technological improvements (e.g., prior removal of CH_4) can be implemented to improve their reliability such options should be further considered.

- An unacceptably high fraction (10 to 35 percent) of urban HCs remain unidentified. Additional research efforts especially with the GC-MS should be conducted to reduce this to less than 5 percent. Until then, specific methods to deal with unidentified HCs should be developed for air quality model applications

- To date, C_2 to C_6 HCs have been measured with packed columns and many small peaks (e.g., butenes) are inadequately resolved. Capillary columns should be tested for the analysis of C_2-C_6 HC species to better resolve these light HC species.

- Currently, oxygenated HCs are measured with questionable accuracy. Additional research, especially for the analysis of aldehydes, is highly recommended. Even though aldehydes may constitute only a small fraction of total NMHC (<5 percent) , their impact on smog formation can be disproportionately large.

- Preliminary analysis of available (Appendix) data indicates that the C_2-C_5 HC fraction, which is also the easiest to measure, is a relatively good indicator of total NMHCs and the associated chemical groups. Because of the tremendous simplification this brings, detailed studies should be performed to analyze available HC species data to test, improve and verify this concept. We recommend that these analyses also include meteorological factors to further improve C_2-C_5 HC relationships with total NMHCs and individual chemical groups. Such data analysis should also be used to better define the unknown HC fraction in various regions.

Appendix

ANALYSIS OF AVAILABLE AMBIENT HC SPECIES DATA

A program of detailed HC species analysis requires expensive instrumentation, experienced personnel, and much time, at best. To test whether a select group of easy-to-measure HCs can be used to characterize the total NMHC concentration of ambient air and the distribution of groups of HCs (e.g., alkanes, alkenes), detailed HC species data were analyzed from two regions:

- Houston, Texas
- South Coast air basin (SCAB), California.

The Houston data were obtained for summer 1977 from the Research Triangle Institute (RTI) (Denyszyn et al., 1979) and summer 1978 from EPA (Nitz and Martinez, 1980), and the SCAB data were collected in summer 1975 (Mayrsohn et al., 1976). Locations of these sites are shown in Figures A-1 and A-2. For each case four sites were selected and 0600-0900 average data acquired for a period of 10 days per site. The 0600-0900 h integrated average was selected because of the well-established importance of this high emission period in air quality applications. Ten days were randomly selected (in some cases, only 10 days of data were available) and no attempt was made to select only those days with similar wind conditions during this preliminary analysis.

Tables A-1, A-2, and A-3 summarize this information in some detail. The percentages of alkanes, alkenes, C_2H_2, aromatics, and aldehydes, and the standard deviation (σ) associated with these, were calculated based on total identified HCs (INMHC). The percentage of C_2 to C_5 HCs and the associated σ were calculated based on both identified HCs as well as total HCs (identified and unidentified HCs). C_2 to C_5 HCs, which are easily measured, may provide a reliable index of total HCs and their distributions. In addition, total NMHC as well as the total identified NMHC are reported in Tables A-1, A-2, and A-3. The RTI data (Table A-1) did not report unknown HCs.

Tables A-1 through A-3 clearly show that total NMHC concentrations in the range of 0.1 to 3 ppm C were observed. Continuous NMHC monitors that seem to operate well above 0.5 to 1 ppm C would probably produce some unreliable data in the HC concentration range encountered. The need for HC species measurements is therefore clearly justified. Tables A-2 and A-3 further show that 10 to 35 percent of the total NMHC fraction was unidentified in Houston and SCAB, a significant fraction of the total NMHC burden. This unidentified fraction could be a major source of error in the exercise of an air quality model that requires as input details other than total NMHCs.

Table A-1 shows that in Houston in 1977 the NMHCs varied significantly at each site (σ/mean = 75 percent) as well as from site to site; this was not the case with the C_2-C_5 HC fraction, however. At each site (Table A-1) the C_2-C_5 fraction of the NMHC burden had a variability of about 15 to 20 percent. Therefore, in Houston the C_2-C_5 HC fraction was a reasonable indicator of NMHCs. As can be expected, the chemical group concentration varies somewhat more. The largest fraction is alkanes and this varies less than 10 percent. The somewhat large

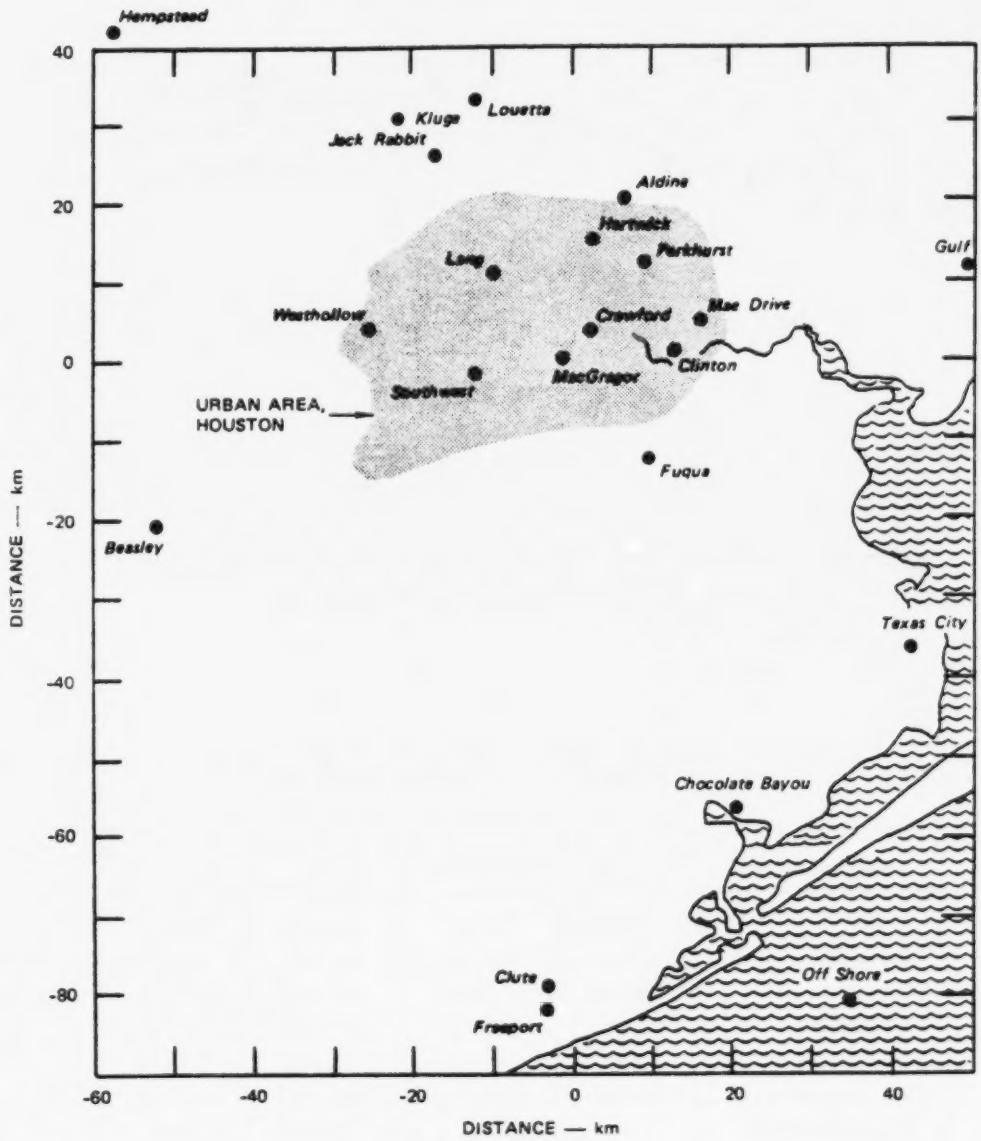


Figure A-1. Locations of selected monitoring sites in the Houston area.

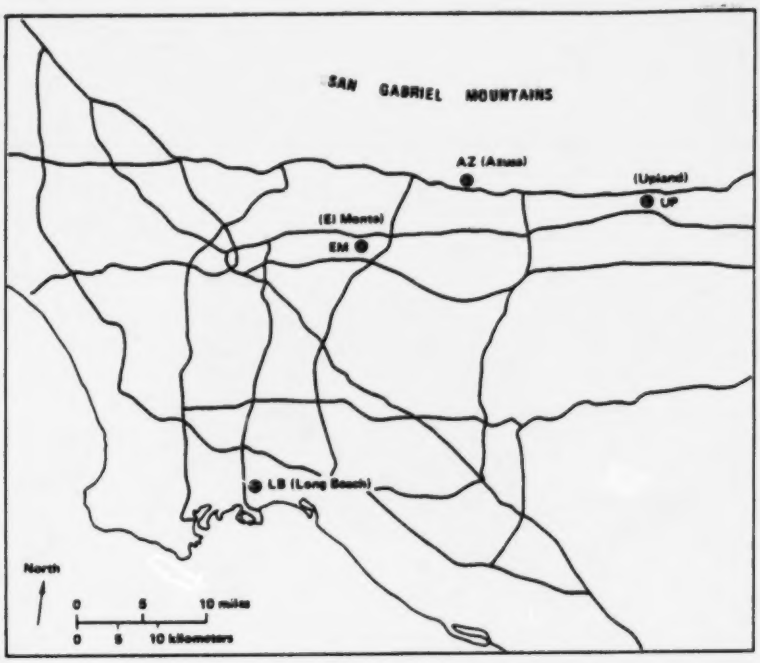


Figure A-2. Southern California sampling sites for 1975.

TABLE A-1. HOUSTON AMBIENT HC COMPOSITION BASED ON DATA COLLECTED BY RTI IN AUGUST-SEPTEMBER 1977

Hydrocarbon Category	Site			
	Aldin Mall	Clinton Drive	Fuqua	Crawford
Alkanes (%)	73.6 ± 5.8*	75.9 ± 5.8	73.4 ± 10.6	72.9 ± 5.4
Alkenes (%)	4.7 ± 1.5	4.4 ± 2.0	5.6 ± 3.8	4.3 ± 0.6
C_2H_2 (%)	4.8 ± 1.3	3.2 ± 1.8	3.6 ± 1.8	5.9 ± 1.9
Aromatics (%)	16.9 ± 5.5	16.6 ± 4.8	17.4 ± 7.5	16.7 ± 6.2
Aldehydes (%)	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
ΣC_2-C_5/ΣINMHC (%)†	63.0 ± 9.5	59.8 ± 11.6	68.7 ± 11.2	55.1 ± 9.3
ΣC_2-C_5/ΣNMHC (%)	—	—	—	—
ΣINMHC (ppb C)	589 ± 448	738 ± 301	574 ± 413	890 ± 356
ΣUINMHC (ppb C)†	—	—	—	—
ΣNMHC (ppb C)	—	—	—	—

*Standard deviation

†I – Identified; UI – Unidentified

TABLE A-2. HOUSTON AMBIENT HC COMPOSITION BASED ON DATA COLLECTED BY EPA IN SEPTEMBER 1978

Hydrocarbon Category	Site			
	May Drive	Crawford	Parkhurst	Lang
Alkanes (%)	70.6 ± 8.2*	61.3 ± 3.2	66.6 ± 5.6	57.9 ± 8.9
Alkenes (%)	10.4 ± 2.8	11.3 ± 1.2	9.1 ± 1.9	11.8 ± 3.3
C_2H_2 (%)	1.8 ± 0.9	3.1 ± 0.5	2.5 ± 0.8	4.6 ± 4.8
Aromatics (%)	16.0 ± 5.0	23.4 ± 2.4	20.2 ± 2.9	24.6 ± 6.3
Aldehydes (%)	1.3 ± 1.3	0.9 ± 0.9	1.6 ± 1.7	1.2 ± 1.1
ΣC_2-C_5/ΣINMHC† (%)	81.9 ± 7.6	51.4 ± 3.7	54.4 ± 5.4	53.3 ± 3.4
ΣC_2-C_5/ΣNMHC (%)	45.5 ± 12.9	41.4 ± 6.3	42.7 ± 9.4	43.8 ± 6.9
ΣINMHC (ppb C)	985 ± 612	1060 ± 472	479 ± 246	736 ± 303
ΣUINMHC (ppb C)†	344 ± 409	308 ± 428	163 ± 262	188 ± 219
ΣNMHC (ppb C)	1329 ± 808	1368 ± 851	642 ± 405	924 ± 384

*Standard deviation

†I – Identified; UI – Unidentified

TABLE A-3. SOUTH COAST AIR BASIN (SCAB) AMBIENT HC COMPOSITION BASED ON DATA COLLECTED BY ARB IN AUGUST-SEPTEMBER 1975

Hydrocarbon Category	Site			
	Upland	Long Beach	El Monte	Azusa
Alkanes (%)	61.9 ± 6.7*	73.4 ± 7.1	66.4 ± 5.7	60.7 ± 4.0
Alkenes (%)	6.3 ± 2.0	5.4 ± 1.0	7.4 ± 2.0	5.9 ± 0.7
C_2H_2 (%)	4.1 ± 1.2	3.0 ± 0.7	4.0 ± 0.6	3.5 ± 0.4
Aromatics (%)	27.7 ± 7.1	18.3 ± 7.5	22.2 ± 6.7	29.8 ± 4.3
Aldehydes (%)	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
ΣC_2-C_5/ΣINMHC (%)†	45.0 ± 12.6	60.4 ± 7.4	52.8 ± 4.1	42.2 ± 3.6
ΣC_2-C_5/ΣNMHC (%)	38.6 ± 12.9	51.0 ± 7.0	43.2 ± 5.9	30.0 ± 6.3
ΣINMHC (ppb C)	1072 ± 887	1066 ± 885	958 ± 999	1189 ± 595
ΣUINMHC (ppb C)†	244 ± 445	160 ± 257	229 ± 273	614 ± 907
ΣNMHC (ppb C)	1316 ± 1240	1066 ± 885	1187 ± 610	1803 ± 1179

*Standard deviation

†I – Identified; UI – Unidentified

variability of the alkene fraction is attributable to the lack of ethylene data, which was estimated based on Washington State University data (Westberg, et al., 1978) [C_2H_4(ppb C)/C_2H_2(ppb C) $\simeq$ 0.74].

Table A-2 from EPA data of 1978 shows very similar behavior.* Once again, C_2-C_5 HCs can be used to represent total identified HCs with an uncertainty of about 10 percent. Total NMHCs, however, are also estimated with an uncertainty of about 20 percent. At each site, the variability of the alkane, alkene, and aromatic fractions is not large. The largest identified fraction is alkanes, which make up about 60-70 percent of the identified HC fraction.

The results from SCAB are nearly the same. Table A-3 shows that the C_2-C_5 fraction can be used to estimate NMHCs with an uncertainty of about 25 percent. At each site the variability of individual chemical groups is quite small and hence it is feasible that these distributions can also be estimated from C_2-C_5 HC fractions.

Because of the great expense involved in the analysis of C_6-C_{12} HCs, we find it highly useful that for a given site C_2-C_5 HCs can be used to estimate total NMHC concentrations with an uncertainty of less than $\pm$30 percent. These variablilities could be further reduced when meteorological details are incorporated (e.g., when days with identical wind directions are considered). These options should be studied in more detail. In practice, a few cases can be analyzed for detailed HCs and, in the remainder of cases, C_2-C_5 HCs used to estimate NMHC and the contribution of individual chemical groups. An uncertainty of $\pm$30 percent is not large when one considers that 15-35 percent of the HC burden is unidentified and measurement errors of the order of 10-15 percent are typical, especially in the analysis of C_6-C_{12} HCs.

Preliminary results of our analysis appear encouraging. More detailed analysis of available data should be conducted to further verify and refine these simplification procedures. Comparison of HC species data for days with similar meteorological conditions would be revealing.

*Here it is not our intent to compare EPA 1978 Houston data with RTI 1977 Houston data. Internal discrepancies are mostly attributable to measurement problems rather than a significant change in the air mix. As an example, the RTI benzene/toluene ratio was highly unusual. In addition, ethylene data from RTI were not available and had to be estimated from a mean C_2H_4/C_2H_2 ratio.

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